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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
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PUBLICATION TO CEASE

The Atomic Energy Commission reluctantly announces that the publication of *Reactor Fuel Processing* will end with the Fall 1966 issue (Vol. 9, No. 4). Argonne National Laboratory will continue limited coverage of this material in a new section in *Power Reactor Technology* beginning with Vol. 10, No. 1.

Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on July 8, 1966.

Reactor Fuel Processing is a Technical Progress Review prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published in this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, G. Bennett, L. Burris, Jr., P. Fineman, A. A. Jonke, G. Kesser, S. Lawroski, W. J. Mecham, P. Nelson, D. Paige, J. Royal, J. Simmons, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subjects reported and for the interpretation of results by the original authors.

Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

By W. J. Mecham and A. A. Jonke

Fuel-Processing Plans

The Eurochemic Plant at Mol, Belgium

The Eurochemic nuclear fuel-reprocessing plant at Mol, Belgium, is almost complete and is undergoing testing. Some reprocessing contracts have been signed, and several tons of fuel elements have arrived.[1]

Eurochemic is an international shareholding company formed in 1959 under the auspices of the European Nuclear Energy Agency by its 13 member countries; Austria, Belgium, Denmark, France, Federal Republic of Germany, Italy, The Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, and Turkey. Some of the member countries have transferred shares to private firms with interests in fuel processing. The initial capital investment in the plant of 21.5 million European-monetary-agreement units of account (EMA u/a) was based on the preliminary cost estimate of 1957. Two increases[1] have been made since, and the capital now stands at 35.75 million EMA u/a.

Main features of the plant design, scope, and initial economic prospects have been presented in earlier issues of *Reactor Fuel Processing*.[2–6] A comprehensive description of the plant and its expected future contribution to the nuclear fuel-processing industry in Europe has been given recently in a series of papers on plant capacity,[1] nuclear safety,[7] main solvent-extraction separation steps,[8] final solvent-extraction cycle for purification of plutonium or highly enriched uranium,[9] instrumentation applications and developments,[10] and waste management.[11]

Eurochemic is a flexible, multipurpose plant that will be able to reprocess fuels discharged from the reactors of its 13 member countries. Chemical decladding methods have been adapted and developed to cope with aluminum, magnesium, stainless-steel, and zirconium type claddings, and Purex type flow sheets have been developed to deal with a variety of uranium fuels of enrichments from natural uranium to 93% ^{235}U. The plant employs pulse columns for the main extraction cycles and mixer–settlers for final purification of plutonium and highly enriched uranium. The design throughput is about 5 kg of uranium per day for the highest enrichment and 400 kg of uranium per day for power-reactor fuels of enrichments of less than 5% ^{235}U. For the latter fuels the capacity can easily be extended to more than 1000 kg of uranium per day. During the next five years, recovery of uranium valued at $25 million, based on the ^{235}U content, is expected.

For the present calculations of expected processing load, only reactors already in operation and reactors under construction or for which construction is definitely committed are taken into account. Those reactors such as the French and British natural-uranium gas-cooled reactors, whose fuels are unlikely to be processed by Eurochemic, are not included. About 30 reactors are considered in estimating the processing load. Of these reactors, 6 are prototype power reactors and 5 are actual power-producing reactors, each of the latter discharging about 10 tons of uranium per year. Four of the reactors are materials-testing reactors with considerable outputs of highly enriched uranium, and the balance are research reactors with relatively small throughput of fissile material. A summary of the expected uranium processing in the period up to 1970 is given in Table I-1.

Table I-1 EXPECTED URANIUM PROCESSING LOADS AT EUROCHEMIC: CUMULATIVE LOADS[1] UP TO YEAR 1970

Reactor fuel	Initial enrichment, %	Average residual enrichment, %	Total uranium output, tons	^{235}U, kg
Natural uranium	0.7	0.5	80	400
Slightly enriched uranium	Up to 1.5	1.1	60	700
Enriched uranium	1.5–5	2.0	70	1400
Highly enriched uranium	5–93	83 to 87	1	900

The plutonium to be recovered by 1970 at Eurochemic will be worth at least $9 million. It can be used in development work for fast breeder reactors or can be recycled to thermal reactors. A summary of the expected plutonium processing load in the period up to 1970 is given in Table I-2.

AEC To Purchase Uranium Concentrate

A uranium-concentrate purchase contract was executed in March 1966 by the U. S. Atomic Energy Commission (AEC) and Continental Mining & Milling Com-

Table I-2 EXPECTED PLUTONIUM PROCESSING LOADS AT EUROCHEMIC: CUMULATIVE LOADS[1] UP TO YEAR 1970

Reactor fuel	Initial enrichment, %	Plutonium produced, kg
Natural uranium	0.7	200
Slightly enriched uranium	Up to 1.5	300
Enriched uranium	1.5–5	400
Highly enriched uranium	5–93	Negligible

pany, which is acquiring the mill at Lakeview, Oreg., formerly operated by Lakeview Mining Company.[12] The mill previously had been closed since November 1960.

The contract provides a market for uranium ores produced through Dec. 31, 1966, from mining properties having AEC allocations issued pursuant to the Commission's announcement of Nov. 24, 1958. This announcement provided the domestic uranium industry with a continuing market in the 1962–1966 period for uranium concentrates derived from ore reserves developed as of the date of the announcement.

The contract permits sale to the AEC of a maximum of approximately 230,000 lb of U_3O_8 in concentrates derived from ores from certain mining properties to be leased by Continental. The price will be $8.00 per pound of U_3O_8 in acceptable concentrates.

AEC Approves Five Foreign Barter Proposals

The AEC announced that it has approved barter fuel-supply arrangements for five power-reactor projects in three European countries.[13] No further barter arrangements will be considered. Two of the approved projects are in Spain, two in West Germany, and one in Switzerland. Under these barter arrangements the United States will accept quantities of natural uranium equivalent to the quantity required to produce the necessary enriched uranium as partial payment for each project. The remaining charges will be paid for in cash.

The five reactor projects are:

ZORITA, a 153-Mw(e) pressurized-water Spanish reactor owned by Union Electrica Madrilena

NUCLENOR, a 440-Mw(e) boiling-water Spanish reactor owned by Santa Maria de Garona de la Compania Nuclenor

KRB, a 232-Mw(e) boiling-water West German reactor owned by Kern Kraft Werk–RWE–Bayern Werk, fuel supplied through Euratom

VEW, a 250-Mw(e) boiling-water West German reactor owned by Vereinigte Elektrizitats Werke Westfalen, fuel supplied through Euratom

NOK, a 350-Mw(e) pressurized-water Swiss reactor owned by Nordostschweizerische Kraftwerke AG Baden

With the approval of barter for these five projects, the AEC does not plan to extend these special fuel-supply arrangements to any additional projects. Of course, enriched uranium will continue to be available from the AEC under its normal policy of sale. In addition, enriching services will be available beginning Jan. 1, 1969, for domestic projects and overseas projects. The commission expects that this will permit new projects abroad not yet under construction to obtain most, if not all, of their fuel inventory by toll enrichment.

Commercial Plutonium Fuel Conference

Programs by industrial firms for promoting the commercial utilization of plutonium as a nuclear fuel constituted the major subject for discussion at the Commercial Plutonium Fuel Conference, Mar. 1–2, 1966, in Washington, D. C.[14–16] The sponsors of the conference were the Atomic Industrial Forum (AIF), the Edison Electric Institute (EEI), and the American Nuclear Society (ANS). The industrial programs of the EEI were outlined by Harvey A. Wagner of the Detroit Edison Company.

The background to the discussion of plutonium utilization was provided by an estimate of the quantities of plutonium to be recovered from commercial U. S. power reactors through 1975. The estimates, shown in Table I-3, were presented by Russell E. L. Stanford and Charles E. Moore of Nuclear Fuel Services, Inc., and were described as an updating of the EEI's 1964 forecast. Utilization of plutonium in both thermal and fast reactors was discussed at the conference. However, fast reactors were not expected to enter the commercial field in the near future.

Table I-3 ESTIMATE[14] OF PLUTONIUM TO BE REMOVED FROM FUEL DISCHARGED FROM COMMERCIAL U. S. POWER REACTORS THROUGH THE YEAR 1975

	Plutonium discharged, kg	Plutonium recovered, kg	
		By year	Cumulative
To 1967	700	499	499
1967	181	59	558
1968	366	337	895
1969	844	499	1,394
1970	870	625	2,019
1971	1,841	628	2,647
1972	3,564	1,830	4,477
1973	5,034	3,564	8,041
1974	6,377	5,034	13,075
1975	8,073	6,358	19,433

The EEI program for the recycle of plutonium in thermal reactors is to be carried out in cooperation with General Electric Company and Westinghouse Electric Corp. The first phase of this program will be the "evaluation of significant economical and technical aspects of utilizing plutonium fuel in thermal reactors and investigating and specifying the best method or methods of utilizing plutonium in large water reactors." For these evaluations the EEI will contribute $325,000 to the General Electric study and $375,000 to the Westinghouse study. The second phase of the program, which is to be conditional on obtaining promising results in the first phase, would include designing and fabricating plutonium-bearing fuel elements and irradiating them in commercial reactors.

The objectives of the above program are to be pursued in parallel but on different thermal-reactor types by General Electric and Westinghouse. The total fuel-irradiation program (i.e., the second phase of the program) is planned to require fuel assemblies containing a total of about 70 kg of plutonium, of which about one-half will be furnished by each company. The reactors selected for the irradiations are the Big Rock Point boiling-water reactor (General Electric) and the Yankee pressurized-water reactor (Westinghouse). Presumably because recycle plutonium of somewhat different isotopic distribution is generated in the above two types of reactors, plutonium of the appropriate source is to be provided for each reactor irradiation.

Plans were announced by the EEI concerning fast breeder reactor research and development. The EEI will promote (but not itself contribute to) a program focused on the Enrico Fermi reactor (Detroit Edison Company), and they planned to demonstrate the performance and operating characteristics of plutonium oxide–uranium oxide fuel. The first phase of this program has as its objectives a preliminary core design and hazards analysis, an examination of the need for critical experiments to determine sodium void and Doppler coefficients, and preparation for irradiation tests. The second phase would involve buying a complete new oxide core for the Fermi reactor.

New Nuclear Power Installations

The total power of new U. S. commercial nuclear reactors ordered in 1965 was greater than in previous years. By the end of the year, the list of 1965 orders and all but final commitments represented an installed nuclear generating capacity of about 4170 Mw(e), based on the appropriate nominal net ratings of the seven plants:[17]

	Mw(e)		Mw(e)
Indian Point No. 2	873	Millstone Point	549
Dresden No. 2	715	Brookwood	450
Turkey Point No. 3	652	Public Service of Colorado	330
Boston Edison	600		

The 1965 list may also include an additional Turkey Point unit, in which case the total installed capacity of the eight reactors would be more than 4800 Mw(e). The possibility that reactors having an even larger total generating capacity will be ordered in 1966 has been reported.[18]

AEC Adopts Amendments to Indemnity Regulations

The AEC has approved amendments to its regulations concerning the levels of financial protection required of licensees who operate large nuclear power plants and who are indemnified by the Commission.[19] These amendments implement recent changes in the Atomic Energy Act.

The Commission must, by law, require financial protection of each organization it licenses to operate a nuclear reactor or other "production or utilization facility," and the AEC must indemnify these licensees against public liability. Financial protection usually is in the form of public liability insurance. Indemnity applies to liability in excess of the insurance carried by the licensees. Financial protection is not required of nonprofit educational institutions and federal agencies, even though they are indemnified under the law.

Public Law 89-210, approved by President Johnson on Sept. 29, 1965, extends the Price–Anderson provisions of the Atomic Energy Act to Aug. 1, 1977. It also provides that the amount of government indemnity—$500 million per nuclear incident—shall be reduced by the amount that the insurance a licensee is required to furnish exceeds $60 million.

The two nuclear energy liability insurance pools (Nuclear Energy Liability Insurance Association and Mutual Atomic Energy Liability Underwriters) have stated that effective Jan. 1, 1966, they will be able to increase the maximum amount of privately available insurance from $60 million to $74 million.

Evaluations of Methods for Uranium and Plutonium Measurement

Statistical evaluations of methods for measuring the chemical concentration and isotopic composition of uranium and plutonium in various forms and materials have been made at the request of the AEC's Division of Nuclear Materials Management.[20] The evaluation program was undertaken to determine the precision and accuracy of each method by its use in different laboratories under varying conditions. Evaluations of methods for determining the presence of impurities in plutonium and uranium also were included in the study.

Results of the evaluations, which are expected to be of assistance to government and private laboratories engaged in plutonium and uranium measurement, have been published in a book entitled *Evaluation of the Methods in TID-7029, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle.** The AEC report, TID-7029, was published in 1963 and described a total of 44 analytical methods.

Rare-Earth Information Center

A Rare-Earth Information Center has been established at the AEC's Ames (Iowa) Laboratory for col-

*A copy of *Evaluation of the Methods in TID-7029, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle* may be obtained[20] from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Va. 22151. The price is $4.00.

lecting, storing, evaluating, and disseminating technical information.[21] The Laboratory is operated for the AEC by Iowa State University. The new center will prepare technical articles, answer requests for information, and publish a newsletter. A file of journal articles, reports, books, and translated foreign articles on rare earths will be maintained, and bibliographies will be made available. The center will serve as the international focal point for information on these metals. Initial emphasis will be on the physical metallurgy and solid-state physics of the metals and their metallic and semimetallic alloys.

The services of the Rare-Earth Information Center are available to governmental agencies, research and educational institutions, and industry. Information may be obtained by calling 515-294-2272 or by writing Dr. Karl A. Gschneidner, Jr., at the Rare-Earth Information Center, Ames Laboratory, Ames, Iowa 50010.

Economics of the Fuel Cycle

Comparative Costs of Processing Fast Reactor Fuels

An estimate was made at Argonne National Laboratory of cost differentials among alternative cases in the processing of commercial fast reactor fuels in facilities[22] to be operated in about 1980. The conceptual plant components on which the processing costs were based comprised the processing plant, ultimate waste disposal, analytical laboratory, and auxiliary facilities. Other important fuel-cycle costs, such as those associated with the reactor and with fuel fabrication, were not included in the study. Flow sheets and plant designs were specified for each of three fuel types (metal, oxide, and carbide), and estimates were made of capital and operating costs for each of three alternative types of processes: aqueous solvent extraction, fluid-bed volatility, and pyrochemical. For each of the above cases, three sizes of processing plant were considered: a close-coupled plant serving a 1000-Mw(e) fast reactor, a close-coupled plant serving three 1000-Mw(e) fast reactors, and a central processing plant serving ten 1000-Mw(e) fast reactors that would be within a radius of 1000 miles. The analysis included other fuel-cycle costs in addition to those directly associated with processing: out-of-reactor fuel inventory and (in the case of central processing plants) shipping charges for spent fuel. A common set of technical and economic ground rules was adopted for the calculation of costs for the several cases.

Of the ground rules forming the basis of the cost comparison, the following are of special interest:

1. The product of each process was the substance (oxide, carbide, or metal) of the reactor core or blanket in a form suitable as feed for fabrication operations without further chemical conversions.

2. In the reference processes, fission-product decontaminations were higher for the products of aqueous and volatility processing than for pyrochemical processing. In all processes, refabrication of the core fuel required at least semiremote techniques because of the hard radiation from the fuel actinides themselves. (Fuel-fabrication costs, not estimated in this study, would be higher for recycle fuel prepared by low-decontamination processes. The evaluation of cost penalties for the low-decontamination pyrochemical process is to be included in a future publication describing the complete study.)

3. The ultimate disposal of high-level radioactive waste as solids was taken as the reference method. However, because of present uncertainty as to the cost of solidification of aqueous waste, disposal costs for aqueous reprocessing wastes were calculated on the basis of perpetual on-site storage of concentrated waste solutions, with the expectation that technical developments in aqueous-waste disposal would ultimately permit solid storage at an equal cost.

Conceptual flow sheets adopted in this study as a basis for developing cost estimates are considered representative of advanced aqueous, volatility, and pyrochemical processes that could be expected to be operational by about 1980. Although each flow sheet was an assemblage of individual steps believed to be feasible in the light of laboratory and pilot-plant data, none of the processes has been fully demonstrated with high-enrichment high-burnup fuel. An analysis of process feasibility was not included in the summary report but is to be included in a future publication that will be the complete report of the study.

For each case of fuel type, process type, and plant size, estimates were prepared of the investment in process equipment and building and in auxiliary facilities and spare equipment based on requirements established for the flow sheets and processing specifications. Construction overhead, plant startup, and working capital were calculated from these estimates.

The annual charge on capital was calculated as the sum of two components: the return on capital and the repayment of capital. The return on capital was calculated as 13% of the total capital investment. The out-of-reactor fuel inventory was charged as a separate nondepreciating item at the rate of 13% per year. The fuel values employed were $10 per gram for ^{239}Pu and ^{241}Pu. No value was assigned to other actinides. The other component of capital cost, the repayment of capital, was calculated as the sum of annual charges on sinking funds at the 6.75% interest rate per year to recover the original amounts of depreciating capital items over their respective economic lifetimes, which ranged from 2 to 30 years.

Estimates were made of the annual operating costs. These included costs of direct labor, indirect labor for maintenance and analytical laboratory operations, and materials (including reagents and utilities) based on specific plant requirements.

Total annual costs were calculated for each alternative case as the sum of: the total annual operating cost, the annual amount for capital repayment, and the annual return on capital investment. The electrical unit costs in mills per kilowatt-hour (electrical) were calculated from the total annual costs for the annual electric-energy production at 80% plant factor for the reference reactor power. The estimates of electrical unit costs are summarized in Table I-4 for the three fuel types, the three processes, and the three plant sizes, and are used as a basis for comparison. The cost associated with an assumed 1% plutonium loss was shown to indicate its relative magnitude.

Because this study had the objective of elucidating cost differences and not predicting actual costs, the chief result was the quantitative estimate of the cost differences. In Table I-5 the differences of the sums of the cost of processing, waste disposal, and out-of-reactor fuel inventory are presented in mills per kilowatt-hour (electrical) along with estimates of the uncertainty of unit-cost differences.

The differences of costs for different processes (Table I-5) indicated that both pyrochemical processing and volatility processing were more economical than aqueous processing for all fuel types for the two sizes of close-coupled processing plants. For the large central plant, the cost estimates also showed that the nonaqueous processes were more economical than aqueous processes for all fuels, but the cost differences were smaller and, in some cases, not significant by the test of significance applied in this study.

For oxide and carbide fuels, the cost differentials indicated that both volatility and pyrochemical processing were more economical than aqueous processing for the close-coupled plants. For the large central plant, volatility showed a significant cost advantage over aqueous processing. The cost differences between volatility and pyrochemical processing were not significant for the ceramic fuels.

For metal fuels the greatest cost advantage was shown by pyrochemical processing for all three sizes of plants. This cost difference of pyrochemical pro-

Table I-4 UNIT-COST SUMMARY[22]

Fuel type	Cost component	Close-coupled plant for 1000-Mw(e) reactor			Close-coupled plant for reactors with 3000-Mw(e) capacity			Central plant for reactors with 10,000-Mw(e) capacity		
		Aqueous	Volatility	Pyrochemical	Aqueous	Volatility	Pyrochemical	Aqueous	Volatility	Pyrochemical
Oxide	Processing	0.53	0.35	0.44	0.29	0.21	0.25	0.16	0.14	0.18
	Waste disposal	0.15	0.09	0.09	0.12	0.08	0.08	0.10	0.08	0.07
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping							0.050*	0.066*	0.071
	1% plutonium loss	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
	Total	0.87	0.58	0.67	0.54	0.37	0.41	0.44	0.38	0.42
Carbide	Processing	0.62	0.43	0.46	0.33	0.26	0.26	0.19	0.17	0.19
	Waste disposal	0.15	0.09	0.09	0.12	0.08	0.08	0.10	0.08	0.07
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping							0.050*	0.066*	0.071
	1% plutonium loss	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
	Total	0.96	0.66	0.69	0.58	0.42	0.42	0.46	0.41	0.43
Metal	Processing	0.59	0.39	0.29	0.32	0.24	0.17	0.18	0.15	0.12
	Waste disposal	0.15	0.09	0.06	0.12	0.08	0.05	0.10	0.08	0.05
	Inventory	0.17	0.12	0.12	0.11	0.06	0.06	0.109	0.079	0.079
	Shipping							0.050*	0.066*	0.071
	1% plutonium loss	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016	0.016
	Total	0.93	0.62	0.49	0.57	0.40	0.30	0.46	0.39	0.34

*Revised after publication of Ref. 22.

Table I-5 SUMMARY OF UNIT-COST DIFFERENCES FOR ALTERNATIVE PROCESSES[22]

Fuel type	Process pairs evaluated		Unit-cost difference* for the sums of processing and waste disposal and inventory, mills/kw-hr†		
	Process A	Process B	Close-coupled, 1 reactor, 1000 Mw(e)	Close-coupled, 3 reactors, 3000 Mw(e)	Central plant,‡ 10 reactors, 10,000 Mw(e)
Metal	Aqueous	Volatility	0.319 ± 0.133	0.174 ± 0.082	0.067 ± 0.055
	Aqueous	Pyrochemical	0.446 ± 0.124	0.271 ± 0.074	0.123 ± 0.050
	Volatility	Pyrochemical	0.125 ± 0.090	0.097 ± 0.059	0.056 ± 0.043
Oxide	Aqueous	Volatility	0.304 ± 0.121	0.169 ± 0.075	0.066 ± 0.051
	Aqueous	Pyrochemical	0.206 ± 0.130	0.129 ± 0.079	§
	Pyrochemical	Volatility	§	§	§
Carbide	Aqueous	Volatility	0.310 ± 0.139	0.166 ± 0.086	0.0611± 0.057
	Aqueous	Pyrochemical	0.279 ± 0.141	0.167 ± 0.085	§
	Pyrochemical	Volatility	§	§	§

*Unit cost of process A minus unit cost of process B.
†To convert estimates to dollars per kilogram, multiply by 308.
‡Shipping costs are included in the cost differences presented for the central plant only.
§The cost difference was judged to be not significant.

cessing with respect to both aqueous and volatility processing was significant for all plant sizes. Volatility processing was significantly more economical than aqueous processing for plants of all sizes.

In Fig. I-1 is shown, for each fuel type and process, the combined unit cost for processing, waste disposal, out-of-reactor fuel inventory, and shipping of spent fuel as a function of the number of reactors served. The shipping charge is applied to the central plant but not to the close-coupled plants, and therefore the cost comparisons in Fig. I-1 show this effect in addition to the effect of plant scale.

In the cases shown in Fig. I-1, a reduction of about 40% of unit costs was found for the increase of size from the case of 1 close-coupled reactor to the case of 3 close-coupled reactors. This result appeared for all types of processing and for all fuels. For the further increase in size accompanying the transition to the case of the central, 10-reactor plant, the unit costs of the aqueous plant incurred a reduction in unit costs of about 40%, a proportional reduction similar to that for the previous threefold increase in size for the close-coupled reactors. For the sum of cost components shown in Fig. I-1, the volatility and pyrochemical plants showed no decrease or, in some cases, an increase in unit costs for the transition from the 3- to the 10-reactor plant. This was due to the higher costs of shipping shorter cooled spent fuel. The shipping charges, where made, included estimates of property and liability insurance for shipment.

For each fuel type shown in Fig. I-1, comparison of close-coupled and central processing plants indicates the following:

1. Aqueous processing is not competitive with volatility or pyrochemical processing for close-coupled plants of the sizes considered in this study. If aqueous processing were chosen, the promising application would be only for quite large central plants.
2. Economic incentives are small for building a large central plant, since nonaqueous processing plants of about one-fourth the size offer the same unit costs for a much lower required investment.

The effects of throughput on processing and waste-disposal costs (i.e., in the absence of inventory and shipping charges) are described in the report.[22]

The basic cost advantage of the nonaqueous processes was related to the fewer process operations and the more compact processing equipment. This had several sources: (1) the much smaller amount or absence of diluents in fuel processing, (2) the simpler accommodation of fuel of high fissionable content and high burnup owing to the absence of reagents offering neutron moderation and suffering irradiation damage, and (3) the direct-process yield of solid actinide products and of concentrated solid radioactive waste. Substantial savings in the cost of shielded process cells and buildings as well as in process equipment accrued because of the more compact equipment.

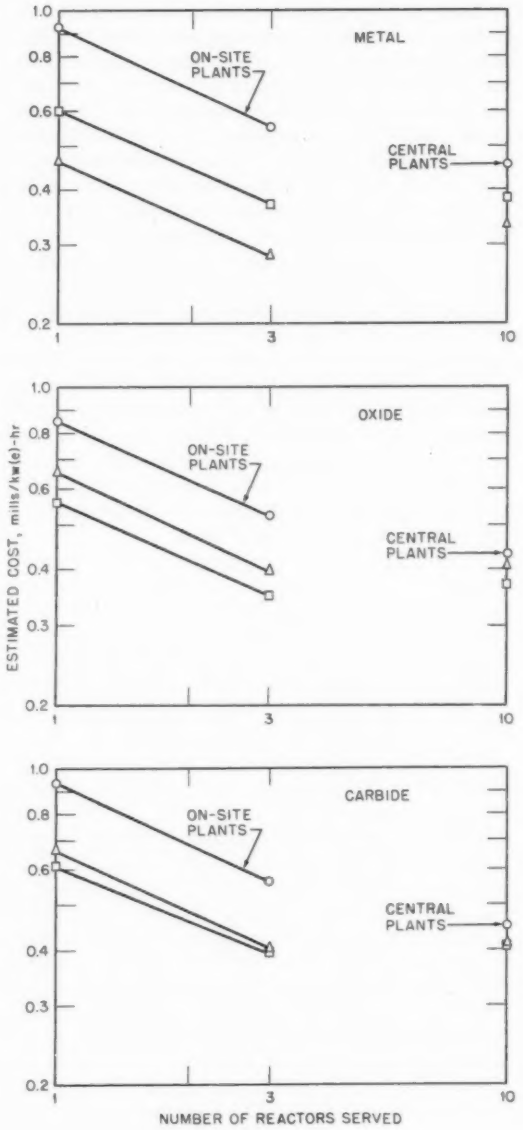

Fig. I-1 Sum of estimated unit costs for processing, waste disposal, out-of-reactor fuel inventory, and shipping of spent fuel for facilities serving 1, 3, and 10 fast reactors of 1000 Mw(e) each. Costs for shipping of spent fuel are included in the 10-reactor case only.[22] ○, aqueous processing. □, volatility processing. △, pyrochemical processing.

Significant savings were also found for the nonaqueous processes in the charges for out-of-reactor inventory. For the purely batch operations that are characteristic of the pyrochemical process, the low inventory costs were due to the short cooling time and the overall rapid processing schedule. For the volatility process the short cooling time and the rela-

tively small holdup of material in the processing equipment allowed similarly low inventory charges.

The sums of unit costs for processing, waste disposal, inventory, and shipping for the cases of this study indicated nonaqueous processes to be 24 to 49% cheaper than aqueous for the close-coupled plants and 5 to 27% cheaper for the central plants.[22]

Economic Aspects of Radioactive-Waste Storage from AEC Fuel-Processing Plants

At the request of the AEC Division of Production, an examination was made by Hanford, Savannah River, and Idaho operations of the long-range financial implications of continuing with present tank storage practices for the highly radioactive-waste effluents from the irradiated fuel-processing plants at each site.[23,24] Comparison was made with certain alternative conceptual procedures for waste management. The total waste-management problem pertains to all the accumulated waste from the aqueous processing of AEC production and testing reactors from initial operations to date, plus waste that will be generated up to 1972. The accumulated waste consists of millions of gallons of solutions and slurries stored at the respective sites. The alternatives considered were those appropriate to the respective sites and were to take advantage of existing facilities insofar as possible. The alternatives consisted, in general terms, of (1) tank storage (the present method or a modification of it), (2) waste calcination, (3) radionuclide fixation, (4) waste evaporation, and (5) waste fractionization. Waste disposal for long-term storage and surveillance of radioactive wastes were also part of the investigation.

In terms of annual expenditures, the investigations of this problem at the three sites indicated, in general, that increased use of an immobile form (solid) for permanent waste storage was less expensive than continuing the present practice of liquid storage, because of the long-range costs of (1) new generations of storage tanks and (2) continuing surveillance and transfer of these liquids for the hundreds of years that they will be a hazard.

When the costs were compared on a present-worth basis (interest of 4% per year), indications were that immobilizing the bulk of the waste as solid in the present tanks would be the least expensive alternative for Savannah River and Hanford, but, for Idaho, the cost of continuing to store the acidic waste liquors in stainless-steel tanks would be lower. These indications resulted from the use of highly theoretical assumptions and calculations and are specific for the ground rules and for the sites involved.

Although the investigation of waste management of AEC large-scale operations does not constitute any general formula or AEC policy, certain technical and economic aspects of waste-disposal alternatives were highlighted:

1. There appeared to be a consensus on the desirability of solid rather than liquid storage for safety and for long-range economic considerations.
2. The formation of sludges in the present high-level liquid-waste storage tanks at Savannah River and Hanford offers difficulties when solutions are to be transferred to new tanks, as is required to maintain long-term tank integrity. However, the use of high-velocity jets of water to resuspend the sludges and pumps to remove the resulting slurry is being tested at Savannah River.
3. Although in-tank solidification of wastes is generally favored on overall considerations of economics and safety, compared to the present storage of liquid, appreciable interim cooling time must be allowed to reduce the heat-generation rate to safe levels in the storage tanks. For example, 110 years of cooling is required for Hanford Purex waste before it can be stored as a cake.
4. For the problem of storage of aqueous wastes as presented to the present AEC sites, installation of additional equipment for various schemes for calcination or fixation of waste as solid involved capital and operating costs which, in the estimation of the investigators, did not show economic advantage compared to containment of solid in the present tanks.
5. Deep storage of wastes in aqueous or solid form in mined caverns has potential merit in avoiding certain hazards of environmental contamination present in the case of near-surface storage, and the mining is relatively cheap. However, interim cooling would still be required and the costs of required underground exploration and the associated research and development could extend into the millions of dollars. If it was determined to be safe for a specific site, this approach would have greater attractiveness when initiated earlier in the life of a high-level activity generation operation. Its attractiveness lies in the promise of negligible surveillance cost.
6. Transportation of high-level wastes to remote storage sites appears to entail appreciable expense. For example, a Savannah River estimate of $33 million was made for moving the calcine resulting from processing its high-level waste accumulation through 1972 from Savannah River to a salt mine in Kansas.

Plutonium and the Long-Range Economics of Nuclear Fuel Costs

The utilization of plutonium in power reactors is a matter of prime concern in the economics of fuel management for future commercial power reactors. The technical status and economic possibilities of using plutonium were reviewed in a paper presented at the 1965 American Power Conference by Wagner of Detroit Edison Company.[25] The basic economic analysis was made in terms of the efficiency of utilization of uranium natural resources that could be achieved by various reactor types using different fuel cycles. In Table I-6 are shown comparisons of reac-

Table I-6 AVAILABLE URANIUM RESOURCES FOR MAJOR TYPES OF POWER REACTORS[25]

Reactor type	Utilization of total uranium resources, %	Maximum economic price of U_3O_8, $/lb	Energy available, Q*
Light water	1–1.5	10	0.1–0.5
Advanced converter	5–10	30	2.3–5.0
Thermal breeder	50	30	23–50
Fast breeder	80	50	270–460

*$Q = 10^{18}$ Btu.

tor types in terms of forecasts of (1) the relative capability of reactor types for utilization of total uranium natural resources, (2) the maximum price that the reactor operator can afford to pay for U_3O_8, and (3) the total energy economically available. The greatest utilization of total uranium resources is given by the plutonium-fueled fast breeder reactor.

Despite its inherently more favorable use in fast reactors, plutonium may be advantageously used as fuel in thermal reactors. An economic incentive for developing such commercial use of plutonium is provided by the fact that the AEC guaranteed buy-back of plutonium will end on Dec. 3, 1970, and other means for the disposition of plutonium must be sought. During the period 1970–1980, the fuel requirements of fast reactors are not expected to be sufficient to consume the plutonium output of commercial power reactors, and the carrying charges for large inventories of stored plutonium are very high when calculated as a 10% per year carrying charge on plutonium valued at $10 per gram. Consequently, if such financial parameters apply, the use of plutonium in thermal reactors appears to be economically desirable during this time period. This application of plutonium in thermal-reactor fuels would also serve to hasten the development of plutonium-fuel-fabrication facilities.

In a paper by Golan,[26] optimum nuclear fuel-resource allocation in the United States was analyzed with reference to the selection of fast reactors and thermal reactors in a nuclear economy using both types. The analysis also compared specific thermal-reactor types, namely, light-water and heavy-water converters and thorium breeders. The principal assumptions that affect the outcome of this analysis were identified as follows:

1. The nuclear power growth rate will follow very closely the estimate made in the AEC *Report to the President 1962*.
2. It was estimated that by 1985 the increase in fast breeder reactors will be limited only by the availability of plutonium for fuel inventories.
3. For fast reactors a total specific inventory was taken, including out-of-core needs, of 2.9 kg of fissile plutonium per electrical megawatt.
4. For fast reactors the net annual breeding gain was assumed to be 5.8%. This figure corresponds to a doubling time of 17 years on the basis of simple accumulation and 12.5 years on the basis of reinvestment.
5. For thermal reactors the values adopted for the ratio of fissile plutonium processed (in open cycle) per ton of U_3O_8 mined were 1.2, 1.5, and 2.5 (kg of plutonium per ton of U_3O_8), respectively, for the reference light-water reactor, the enriched uranium-fueled heavy-water reactor, and the natural-uranium-fueled heavy-water reactor.
6. The uranium inventories (open-cycle operation) adopted were taken as 27.3, 17, and 16 tons of U_3O_8 per 10^9 kw-hr, respectively, for the reference light-water reactor, the enriched-uranium-fueled heavy-water reactor, and the natural-uranium-fueled heavy-water reactor.

On the basis of a set of economic ground rules (summarized in Table I-7), a comparative economic analysis was made for three reference economies, an all light-water reactor economy and two fast reactor economies (A and B) described as follows:

Economy A

Consists of all light-water reactors with plutonium recycle until 1985; after 1985 it consists of a balanced nuclear economy of light-water reactors and plutonium fast breeder reactors.

Economy B

Consists of all light-water reactors with plutonium recycle until 1975; between 1975 and 1985 new nuclear additions are split equally between light-water reactors and heavy-water reactors, both using enriched uranium, and the plutonium produced is recycled into light-water reactors only. After 1985 the economy is a balanced nuclear economy consisting of (1) converters composed of 25% light-water reactors operating on enriched uranium and 75% heavy-water reactors operating on natural uranium, and (2) plutonium fast breeder reactors.

In the balanced economies A and B, it was assumed that the nuclear demand would first be met by the plutonium-fueled fast breeder reactors, depending on plutonium availability, with the balance of the demand met by converter reactors of the assumed type. The basic comparisons for the alternative economies made in this study can be stated as follows: (1) fast breeders are necessary to avoid the large uranium requirements of an all light-water reactor economy; (2) the comparison of fast reactor economies A and B shows a substantial advantage of a combination of fast reactors with heavy-water reactors rather than with light-water reactors alone.

Table I-7 ECONOMIC GROUND RULES IN COST STUDY[26]

Fuel cost	
Cost of U_3O_8, $/lb	8
Separative work, $/kg	30
Conversion of U_3O_8 to UF_6, $/kg U	2.70
Fertile ThO_2, $/kg	11
Fissile ^{233}U, $/g	12
Fissile ^{235}U, $/g, fully enriched	12
Fissile plutonium, $/g	10
Cost of low-enrichment uranium	July 1, 1962: AEC schedule
Costs of fabrication and reprocessing	Based on levels of operations projected for the 1975–1980 period
Total energy cost	
Fixed charges on plant capital, %/year	12
Fixed charges on fuel investment, %/year	10
Fixed charges on D_2O investment, %/year	10
D_2O makeup with organic coolant, %/year	0.5
Annual plant factor, %	80
Cost of D_2O, $/lb	20

The versatility of the heavy-water reactor type, which also can serve as thorium-cycle converters, was cited in the report. However, it was concluded that thorium-cycle converters do not make any significant contributions to resource conservation in an economy in which fast reactors play an important part.

For each of the balanced reactor economies A and B, a maximum cumulative uranium requirement (Fig. I-2) is reached at about the year 2035, when sufficient plutonium is bred to satisfy all requirements for additional fissile material. That is, ^{235}U is no

longer required. For practical purposes the maxima shown in Fig. I-2 may represent the *total* U. S. uranium requirements for many years to come.

Other conclusions of the study were:

1. Any appreciable delay beyond 1985 in large-scale introduction of fast breeders would greatly increase ore requirements, with higher attendant costs to the economy.
2. The use of heavy-water reactors with fast reactors reduces by about one-third the uranium requirement regardless of when fast breeders become available.

Further economic comparison was made in the study between the three reference economies by plotting in Fig. I-3 the estimated cumulative savings for economies A and B from the effects of the following economic functions: (1) the cost of U_3O_8 as a function of the cumulative uranium mined and (2) the differential in the cost of electric power for light-water and heavy-water reactors as a function of the cost of U_3O_8.

In the figure are shown the relative worth of the potential savings of the two balanced fast reactor economies A and B, as compared with an all light-water reactor economy, and with each other. The values[26] are shown as the cumulative present worth (1965 dollars) for the period until the year 2000.

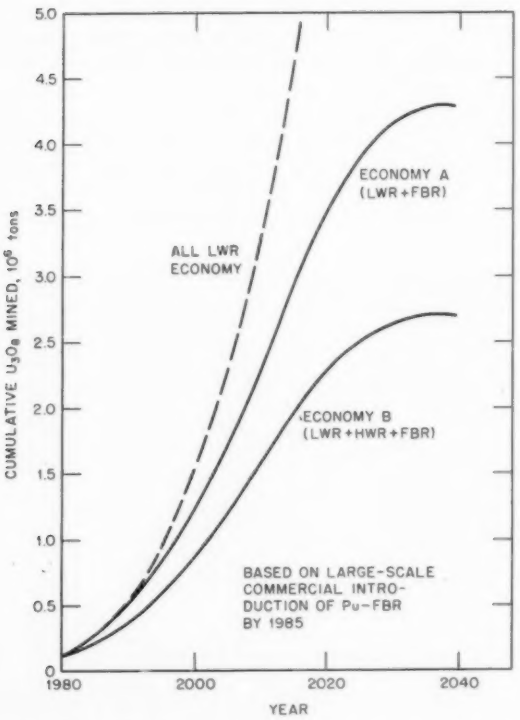

Fig. I-2 Cumulative uranium ore mined vs. time.[26] LWR, light-water reactor; HWR, heavy-water reactor; FBR, fast breeder reactor.

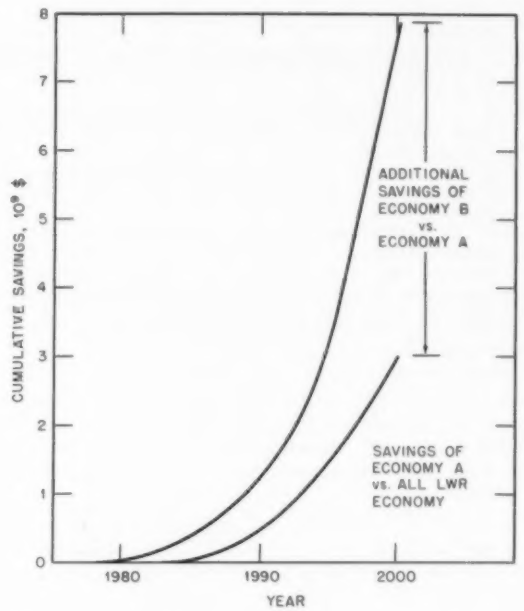

Fig. I-3 Potential cumulative savings (1965 dollars) due to development of fast breeder reactors and heavy-water reactors as compared with light-water reactor economy only.[26]

AEC Patents Available for Public Use

The AEC has continued its practice of making government-owned patents available for public use. The Commission will grant nonexclusive, royalty-free licenses on released patents. Titles and abstracts are published as press releases of the AEC. Copies of the patents may be obtained from the U. S. Patent Office for 25 cents a copy. In announcements not previously cited in *Reactor Fuel Processing*, a total of 375 new patents were made available for licensing. In addition to U. S. patents, those from 12 other countries were included. The patents cover a wide range of items concerning nuclear reactor and fuel-processing operations.[27–36]

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

By C. E. Stevenson and D. M. Paige

Preparation of Zirconium-Alloy Fuel for Processing

Some years ago process equipment was installed at the Idaho Chemical Processing Plant (ICPP) for the dissolution in hydrofluoric acid of Zircaloy-clad zirconium–uranium alloy (containing only a few percent of highly enriched uranium, i.e., seed fuel for the Shippingport Pressurized Water Reactor).[1] The resulting solution was then mixed with $Al(NO_3)_3-CrO_3$ solution to permit uranium recovery and decontamination by tributyl phosphate (TBP) extraction. Process modifications were later developed to overcome or minimize certain limitations, such as low capacity, low percent uranium allowable in the dissolver solution, vessel corrosion, and large waste volume per unit of product.[2,3] The ICPP process equipment has been modified accordingly, and satisfactory operation of the improved process has recently been reported.[4]

The capacity of the dissolution equipment was increased about ninefold by providing for semicontinuous rather than batch dissolution in the tall-pipe Monel dissolver vessel shown in Fig. II-1. As much as 600 kg of zirconium is dropped into the 13-in.-diameter slotted basket suspended in water (to cushion the fall of fuel); the water contains greater than 5 g of boron (as H_3BO_3) per liter as a nuclear poison. The water is removed, and $6.6M-7.3M$ HF, also containing H_3BO_3, is fed continuously to the dissolver, which is held at 60°C for about 12 hr. The continuously overflowing product is fed to an adjustment vessel along with about one-fourth its volume of $2M$ $Al(NO_3)_3$ containing 5 g of chromium per liter; the mixture next passes to a pulsed column for extraction with 10% TBP in a hydrocarbon diluent. The partially decontaminated product is concentrated for further processing. The complete first-cycle flow sheet is shown in Fig. II-2. Following this cycle, decontamination is completed according to customary ICPP practice by two cycles of extraction with hexone.

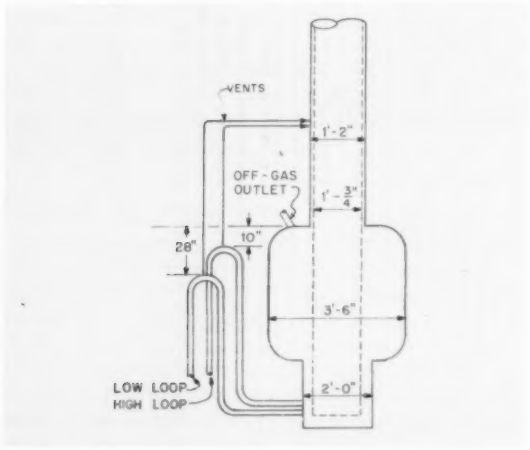
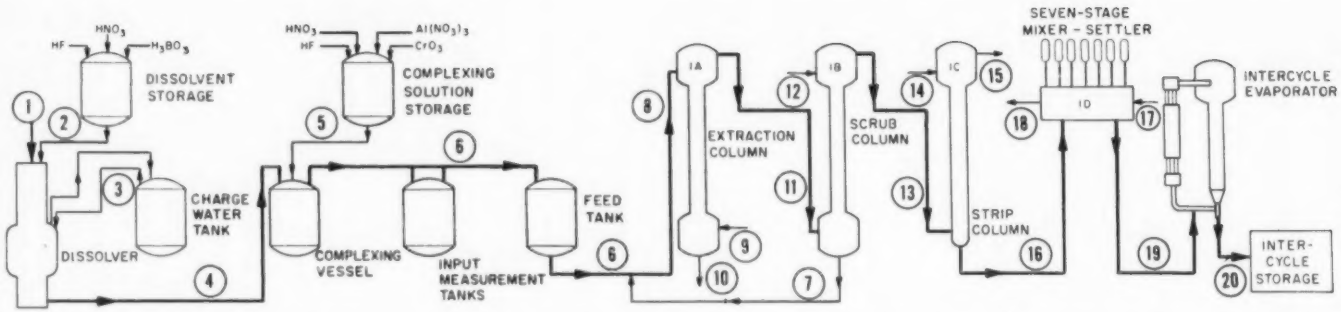


Fig. II-1 Dissolver for zirconium fuels.[4]

The $Al-Zr-F-NO_3$ feed and waste solutions are susceptible to the formation of solid phases if heated or if composition is not closely controlled. Consequently concentration cannot be effected by evaporation, and close control of flow rates is required in the continuous adjustment step.

The use of soluble nuclear poison permits use of a nongeometrically safe dissolver for rapid dissolution of zirconium-alloy fuel by enabling the dissolver to handle a large mass of metal. For control of nuclear safety during dissolution, the presence of ^{10}B in the cushioning water and in the dissolving reagent must be assured. Dual monitoring instruments are provided in the dissolving-reagent feed tank. These automatically cut off the flow of dissolvent if either one shows a deficiency of boron. Initial operation was most satisfactory, and an average processing rate of 764 kg of zirconium per day was maintained over a three-week period. The reaction of zirconium with HF releases hydrogen, which is disposed of by dilution with air to maintain a concentration below the explosive limit. In one instance a minor hydrogen explosion occurred while fuel was being charged into the dissolver.[5] No equipment damage, contamination spread, or personnel injury resulted. This incident was attributed to the reaction of zirconium or aluminum with a small amount of residual acid in the cushioning water in the dissolver. With improved venting and purging of the dissolver, no further difficulty has been encountered.

First-cycle process performance was good. Uranium losses were 0.2 to 0.9% of the input, and aver-



STREAM	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17 and 18	19	20
DESCRIPTION	FUEL CHARGE	DISSOLVENT	CHARGE WATER	DISSOLVER PRODUCT	COMPLEXING SOLUTION	COMPLEXED DISSOLVER PRODUCT	1BR	1AF	1AX	1AR	1AP	1BS	1BP	1CX	1CR	1CP	1DX	1DR	1DP	FIRST-CYCLE PRODUCT
Flow, l/hr		532 (a)		548 (a)	141 (a)	472 (b)	65	537	500	537	500	65	500	225	500	225	10	200	19	
TBP, %									10.0		10.0		10.0		10.0					
Diluent									Amsco		Amsco		Amsco		Amsco		Amsco			
Zr^{++++}, M				1.0		0.75		0.66		0.66										
F^-, M		6.54		6.34		4.75		4.18		4.18										
Al^{+++}, M					2.0	0.38	1.5	0.52		0.52		1.50								
H^+, M		6.78 (e)		2.49 (e)		1.87 (e)		1.60 (e)		1.46 (e)	0.15	1.13 (d)		0.005		0.005		0.005	0.5	
NO_3^-, M		0.03		0.02	6.0	1.17	4.5	1.57		1.42	0.16	3.36	0.01	0.005		0.02		0.02	2.0	
Sn, g/liter				1.42		1.07		0.94		0.94										
Cr, g/liter					4.9	0.95		0.83		0.83										
B, g/liter		4.1	7.0	4.1		3.1		2.72		2.72										
U, g/liter				1.19 (c)		0.82	0.001	0.72		8×10^{-4}	0.77		0.77			1.72		1.72	200	
Density at 25°C		1.03		1.18		1.20	1.23	1.21	0.79	1.20	0.80	1.19	0.79	1.00	0.79	1.00	0.76	1.00	1.27	
U, kg/batch	7.2 (c)																			
Zr, kg/batch	600																			
Sn, kg/batch	9.3																			

(a) AVERAGE RATE FOR A 12-HOUR DISSOLUTION CYCLE.

(b) AVERAGE RATE FOR CONTINUOUS EXTRACTION (24-HOUR DAY). INCLUDES SOME JET DILUTION.

(c) ASSUMES A 40% BURNUP OF URANIUM. (CRITICAL SAFETY ASSURED IN ABSENCE OF BURNUP, i.e., FOR UP TO 16.7 KG OF FULLY ENRICHED URANIUM.)

(d) THE USE OF DIBAN IN THE SCRUB MAKES IT 1.13M ACID DEFICIENT.

(e) TOTAL ACID.

Fig. II-2 Flow sheet for dissolution and first-cycle extraction of zirconium-alloy fuels.[4]

age gross beta and gross gamma decontamination factors of 1000 and 8000 were obtained. Processing through the second and third cycles had not been completed at the time of the report. Flow-sheet modifications also effected a one-sixth reduction of the waste volume per unit weight of zirconium processed, and a 40% reduction in the amount of aluminum salt associated with the zirconium, relative to original process conditions.

One of the process innovations that may be observed in the flow sheet (Fig. II-2) is the use of dibasic aluminum nitrate (DIBAN) in the scrubbing (IB) column. The purpose of using DIBAN instead of $Al(NO_3)_3$ is to permit extraction at reduced salting strength, with a 10% instead of 5% TBP extractant, to obtain the reduction in waste volume noted above. With the higher TBP concentration, greater extraction of HNO_3 could occur, which would result in increased uranium losses in the IC column raffinate. The 1.13M acid-deficient scrub effectively neutralizes HNO_3 and prevents such losses. To provide DIBAN solution for this use, workers developed a process for its production at 2.2M concentration by dissolving metallic aluminum in 0.8M $Al(NO_3)_3$ containing 0.4M HNO_3 and 0.0125M $Hg(NO_3)_2$ (as a catalyst). Such a solution was found to be stable for more than six months, whereas commercially supplied 4M DIBAN degraded rapidly in storage owing to precipitation of Al_2O_3.

Solvent-Extraction Processes

The feasibility of recovering neptunium by solvent extraction in processing aluminum-alloy fuels at the ICPP has been demonstrated. A synergistic effect on the extraction of uranium has been noted for the system trioctylaminediisoamyl phosphoric acid. High radiation levels adversely affect the separation of actinides and lanthanides by extraction with Alamine 336 from a concentrated LiCl solution, but process levels of radiation are tolerable. A solvent-extraction process has been developed for recovery of actinides that might be produced by a nuclear detonation in a salt formation.

Recovery of Neptunium

It has been noted earlier that the recovery of ^{237}Np from irradiated fuels is of considerable interest since reirradiation of ^{237}Np permits the production of ^{238}Pu for use as a long-lived energy source in space vehicles and other remote installations.[6,7] In recent ICPP processing the feasibility of recovering neptunium from the second-cycle hexone-process raffinate from aluminum fuel processing was demonstrated.[8] Recovery methods were based on the observation that initial extraction of neptunium in a quantitative manner requires that it be in the IV or VI valence state rather than in the inextractable V valence state.

In the recent plant-scale studies of neptunium extraction, an initial attempt was made to convert neptunium quantitatively to the IV valence state by the addition of $Fe(SO_3NH_2)_2$ directly to the extraction column (to avoid ferrous ion oxidation). With this modification, only about 20% of the available neptunium was carried into the first-cycle product stream. This method of valence control was not believed to provide adequate time for the reduction of Np(V) to Np(IV); however, other studies[9] have shown that reduction of Np(V) with ferrous sulfamate is nearly complete in a few seconds at ambient temperature.

The alternative of oxidation to Np(VI) is available, however. In future operations it is proposed to effect this by adding chromic acid to the dissolver solution. The feasibility of this technique was felt to have been demonstrated by addition of chromic acid to the accumulated second-cycle raffinate from ICPP aluminum fuel processing run 21, in which over 500 kg of aluminum-alloy fuels from 15 reactors was processed. It is probable that only a portion of the potentially available neptunium was contained in this raffinate since the attempted reduction was relatively ineffective and was carried out for only a part of the run. Analysis indicated that the accumulative raffinate contained about 32 g of ^{237}Np. This solution was adjusted to contain 1.5M $Al(NO_3)_3$, 1.0M HNO_3, and 0.01M CrO_3; and the neptunium was then extracted by an equal volume of 10% TBP in a kerosene type diluent, from which the neptunium was stripped with 0.01M HNO_3. The product solution was then evaporated to a concentration of 4.8 g of neptunium per liter for a total recovery of 28.8 g. In proposed operations this would be further purified by plutonium partitioning and ion-exchange purification, as shown in the flow sheet given in Fig. II-3. Laboratory data have also been obtained to show that neptunium can be recovered from zirconium process feed solutions by oxidation[4] with Cr(VI).

Synergism in Extraction Systems

Synergism in solvent-extraction systems represents an advantageous property of mixed solvent systems characteristic of organophosphate extraction of metal ions. The effect has previously been discussed[10] for solvents composed of dialkyl phosphoric acid and a neutral organophosphate, for which it is noted that extraction coefficients (for UO_2^{2+}, for example) are considerably greater for the mixture than the sum of the extraction coefficients for the individual reagents. The use of such mixtures affords a means of enhancing and controlling extractability of certain metals.

Smelov and Strakhova[11] have recently reported similar synergistic behavior for extraction of $UO_2(NO_3)_2$ by mixtures of trioctylamine (TOA) and diisoamyl phosphoric acid (DAPA) in benzene solution. With an aqueous phase containing 2M HNO_3 and a solvent containing 0.02M TOA, the DAPA concentration was varied from 0.001M to 0.02M. The maximum syner-

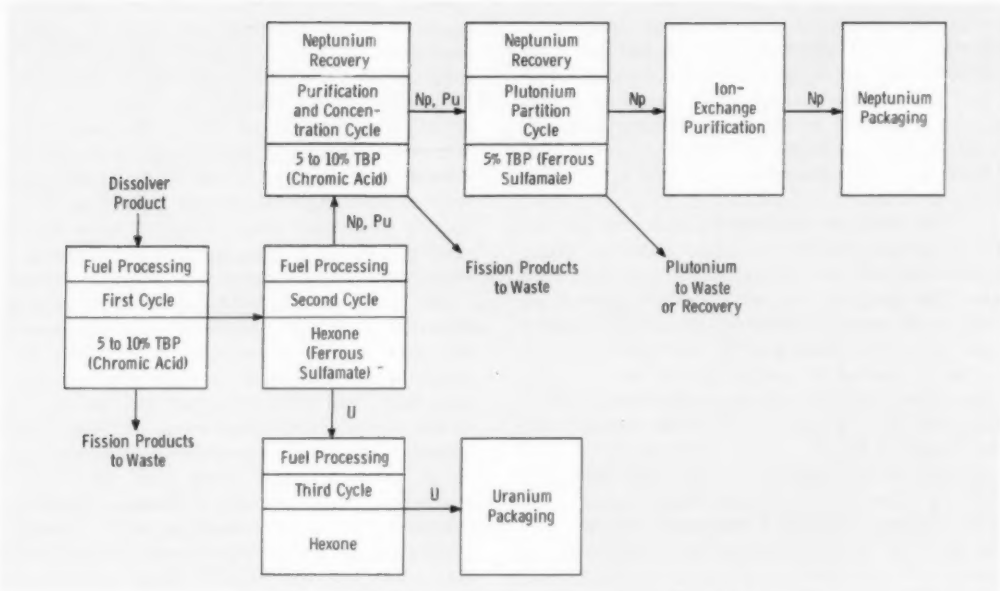


Fig. II-3 Flow diagram for proposed recovery of neptunium at the ICPP.[8]

gistic effect was noted at approximately 0.005*M* DAPA. Similarly, with a fixed concentration of 0.002*M* DAPA in the solvent, the concentration of TOA was varied from 0.002*M* to 0.05*M*, and a peak in synergism was observed at approximately 0.01*M* TOA. This suggested an optimum ratio TOA/DAPA of about 3.5. In further studies the concentration of HNO_3 in the aqueous phase was varied from 0.05*M* to 3*M* using a solvent containing 0.02*M* TOA–0.02*M* DAPA. The greatest synergistic effect here was noted for 0.25*M*–0.5*M* HNO_3. On the basis of this information, the mechanism of extraction was concluded to be as follows:

$$UO_2^{2+} + 2(HAm_2PO_4)_2 + TOA = UO_2(Am_2PO_4)_2 \cdot HAm_2PO_4 \cdot TOA + \tfrac{1}{2}(HAm_2PO_4)_2 + 2H^+$$

and

$$UO_2^{2+} + (HAm_2PO_4)_2 + 2TOA = UO_2(Am_2PO_4)_2 \cdot 2TOA + 2H^+$$

Extraction of Transplutonic Elements

In the U. S. program for the isolation of gram quantities of transplutonic elements,[12] the transuranium processing facility (TRU) at Oak Ridge National Laboratory (ORNL) is expected to play a major part by accomplishing the primary chemical separation of these elements from irradiated target material. A tertiary amine extraction process from LiCl solution has been planned for use in effecting separation of the actinides as a group from the lanthanide fission products.[13] More recently, Weaver and Kappelmann at ORNL proposed to effect this separation by a process based on complexing actinides with an aminopolyacetic acid.[14] Leuze and others have recently reported on experience with application of the Alamine 336–LiCl process at very high activity levels and on development of the alternative process for actinide–lanthanide separation.[15]

The first process operation involves conversion from a nitrate to a chloride system by coextracting actinides and lanthanides with Alamine 336 from a $LiNO_3$-salted solution and stripping back into HCl. This was accomplished satisfactorily with feed containing as much as 440 curies of ^{242}Cm per liter (16 watts/liter). The only detectable effect of irradiation was a very slow loss of acid (< 0.01*M*/liter per day).

The Alamine 336–LiCl extraction process was then used during the isolation of gram amounts of ^{243}Am–^{244}Cm and ^{241}Am–^{242}Cm at activity levels as high as 18 watts/liter. Difficulties attributed to radiation effects were encountered in cerium decontamination and in loss of free acid. In an operation with a feed containing only 20 curies of ^{244}Cm per liter, a cerium decontamination factor of only 8 was noted, compared to a value of greater than 100 for europium. It appeared that the cerium was partially oxidized to the extractable Ce(IV) state since improved cerium decontamination resulted from the addition of 0.1*M* $SnCl_2$ to the feed as a reductant. At higher radiation levels, i.e., 390 curies of ^{242}Cm per liter, the stannous ion was oxidized so rapidly that it was impossible to complete the processing run before it was consumed, and poor cerium decontamination resulted. However, when excess acids and oxidants were re-

moved prior to the addition of $SnCl_2$ and when processing was begun soon thereafter, reasonably satisfactory cerium decontamination was obtained in processing a feed that contained 170 curies of ^{242}Cm per liter at a radiation level of less than 600 watt-hr per equivalent of reductant.

In earlier laboratory studies it had been noted that a loss of acid from the feed solution to the Alamine 336–LiCl process, which accompanied high levels of alpha activity, could be inhibited by the addition of CH_3OH to the feed. However, with actual process feeds this was less successful. For example, with the addition of 5% CH_3OH to a feed containing 67 mg of ^{242}Cm per liter (8 watts/liter) in 12.2*M* LiCl, acidity dropped from 0.3*M* to 0 after an exposure of about 900 watt-hr/liter. This was attributed to the presence of hydrolyzable metal ions that interfered with the protective action of CH_3OH. In later studies it appeared that aging a feed solution several hours before alcohol addition improved the inhibiting action of the alcohol.

The alternative process being developed for actinide–lanthanide separation uses extraction of lanthanides with di-2-ethylhexyl phosphoric acid (D2EHPA) in diisopropylbenzene from a lactic acid solution by complexing the actinides with the pentasodium salt of diethylenetriaminepentaacetic acid (DTPA, used as a scrub in lactic acid) in order to retain them in the aqueous phase. In a second and similar extraction cycle, conditions are adjusted to permit the actinides to be extracted, and separation is thereby effected from other fission products (i.e., ruthenium and zirconium). The potential advantage of this process as compared to the Alamine–LiCl process is the much less corrosive nature of the feed solution. The chloride process requires the use of tantalum, Zircaloy-2, and Hastelloy for equipment and piping, whereas conventional stainless steel could presumably be used for lactic acid systems.

With continued work on the D2EHPA–DTPA process, the actinide–lanthanide separations obtained approach those secured with the tertiary amine separations in chloride systems. Development of an optimum process is inhibited by the variety of conditions that may be adjusted and must be defined. Studies were made on the use of other carboxylic acids to replace lactic acid (glycolic acid, for example). Actinide–lanthanide distribution coefficients and separation factors have been found to be quite sensitive to the *p*H of the system. Some studies were made on the effects of radiation level on this system. They indicated that there was only a slight adverse effect on the separation factor at exposures up to 440 watt-hr/liter.

Actinide Recovery from Nuclear Detonations in Salt

One aspect of the Plowshare Program for development of peaceful uses of nuclear explosives is the production of transplutonium elements in significant quantity by irradiation of a uranium target with neutrons produced by a thermonuclear device.[16] This can be accomplished by carrying out the explosion in a large underground salt deposit. The actinides are recovered by mining and processing the crude salt. From a 10-kt shot, about 5000 tons of salt will be melted, all of which may contain the desired elements, and several times as much additional salt may be spalled from the roof of the cavity together with dirt, rock, and other debris. Karraker and Perkins of the Savannah River Laboratory have recently reported that a feasible chemical process based on dissolution and TBP-diluent solvent extraction of the salt mass has been developed for recovery of about 85% of the actinides present.[17]

The process was developed on the basis of tests with debris produced in the Gnome nuclear explosion near Carlsbad, N. Mex., and the separation and purification of a very small amount of plutonium–curium was actually accomplished. The process was based on the use of such a salt formation located near Carlsbad, N. Mex., where there are thick beds of impure salt separated by thin layers of silt, sand, or clay at 5- to 10-ft intervals. The overall composition of the deposit is about 95% NaCl with minor amounts of such substances as $CaSO_4$, $MgSO_4$, silicates, and iron. The recovery of gram amounts of actinides from such material requires a separation factor of about 10^9.

In the development studies with Gnome debris, 99.4% of the NaCl was removed from the debris by dissolution in water with a loss of only 0.1 to 0.2% of the actinides present to the waste salt solution. Agitation of the residue with $(NH_4)_2CO_3$ metathesized sulfate to carbonate with an actinide loss of less than 1%. Actinides were almost completely dissolved from the water-insoluble residue with 6*M* HNO_3, from which they were recovered by extraction with 30% TBP in a hydrocarbon diluent. Silica was removed, prior to extraction with TBP diluent, by addition of gelatin and filtration.

This process is essentially that recommended for use, as shown in Fig. II-4 (see the next page), with two solvent-extraction cycles and intermediate and final stages of product concentration by evaporation. Concentration factors of 14 and 30 are proposed for the extraction cycles and of 8 to 10 for evaporation. The overall concentration factor from extraction feed to product is then 18,000, which would result in a recovery of about 85% of the actinides initially present.

Ion-Exchange Processes

In nuclear fuel reprocessing, ion-exchange separations have typically been applied to the final purification and concentration of the product (e.g., plutonium[18]) or to the isolation of fission products.[19] In the

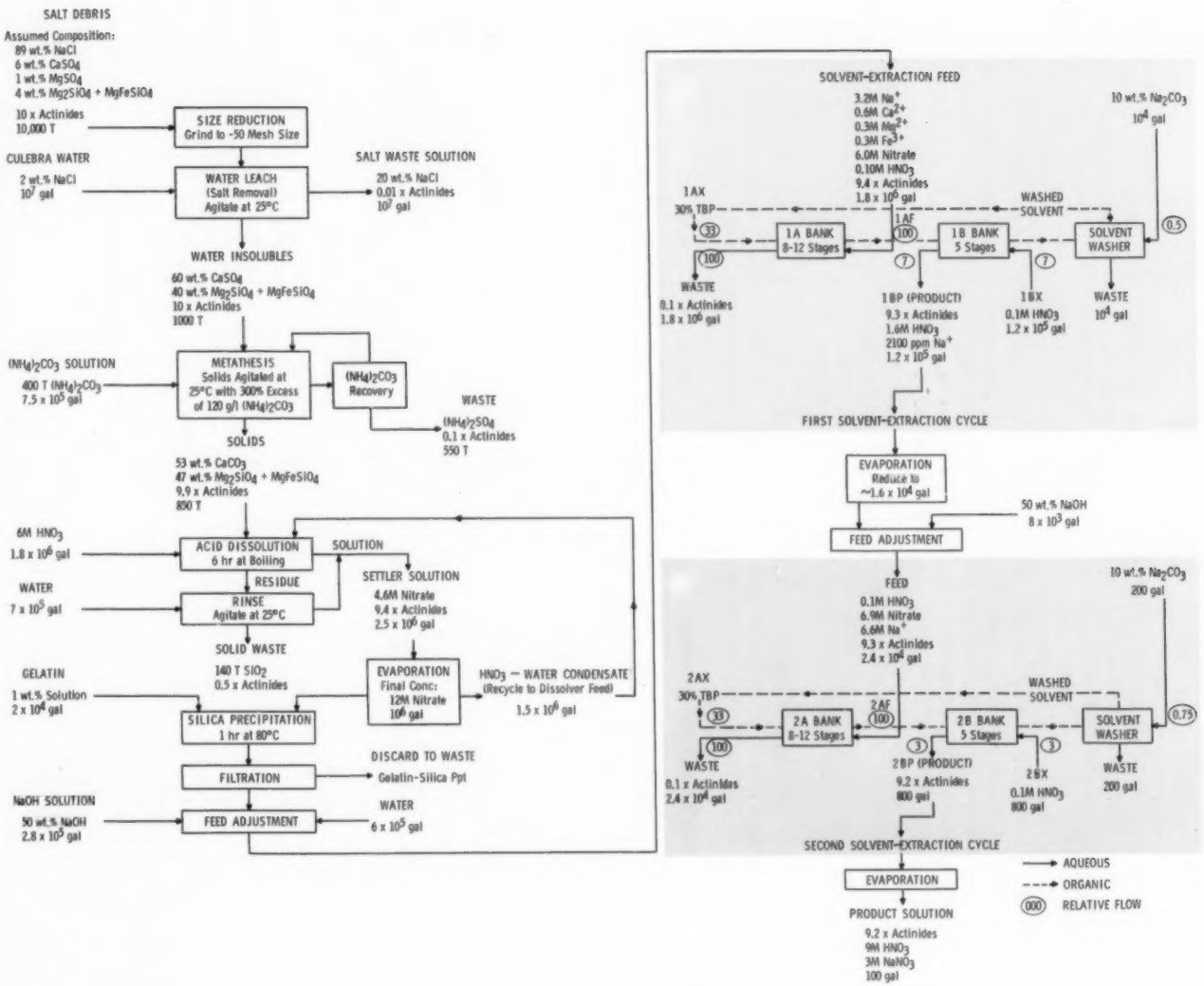


Fig. II-4 Process for recovery of actinides from crude salt.[17]

initial development of alternatives to the precipitation process for plutonium recovery, ion exchange was given serious consideration. Nikashina and others recently reported studies on ion exchange as a technique for the primary separation of irradiated uranium from rare-earth fission products with high cross sections.[20]

Basic to this study was the known effectiveness of ion exchange for the separation of uranium in its ores from rare-earth elements and the normally low concentration of fission-product elements relative to uranium in reprocessing. It was recognized also that, since irradiation effects are of primary importance in the processing of irradiated fuels, the use of organic media or complexing agents, such as oxalic and citric acid, would be undesirable and that the resin to be used should be of a type relatively stable to radiation. For the latter reason the performance of the sulfonated polystyrene cation-exchange resin KU-2 was examined. Ytterbium was chosen as the rare-earth ion whose separation from uranium was to be effected since this small-radius ion has the lowest ion-exchange constant and the greatest tendency toward complex formation of the rare earths and is therefore more difficult to separate from uranium than other rare earths. From data available, calculations were made to indicate the relative sorption of uranium and ytterbium, present in solution at a 40/1 ratio, from $0.0005M$–$0.04M$ uranium solutions at acidities of $0.5N$–$1.5N$, assuming no complex formation; separation factors ranged from 12 to 15. Coefficients of separation were also calculated for fluoride and sulfate systems since these anions form strong complexes with UO_2^{2+}. Very high separation coefficients were indicated for the fluoride systems, and reasonably good separations were indicated for sulfate systems.

Studies of the chromatographic elution of uranium and ytterbium from KU-2 resin were carried out using $0.5N$–$1.5N$ $HClO_4$, HCl, HNO_3, H_2SO_4, and HF solutions. The results are expressed in terms of $V_{max.}$, the eluant volume (milliliters) corresponding to the peak concentration of the ion eluted. This is related to the distribution coefficient, K_D, by the following expression:

$$K_D = \frac{V_{max.} - V_f}{m}$$

where V_f is the free volume (milliliters) in the chromatographic column and m is the volume of wet resin (milliliters). The results for elution with $1M$ acids are given in Table II-1. Since $HClO_4$ is known not to form complexes with uranium, its behavior is characteristic of simple elution. The behavior with HCl and HNO_3 solutions is similar, except that elution of uranium is a little easier, indicating slight complexing. With H_2SO_4 and HF the separation was far more effective, presumably because of the formation of strong complexes. Calculations were carried out assuming complexes of varying composition. Good agreement of calculation and experiment was found for complexes with compositions of UO_2SO_4, $UO_2(SO_4)_2^{2-}$, and UO_2F_2.

Table II-1 CHROMATOGRAPHIC ELUTION OF URANIUM AND YTTERBIUM FROM KU-2 RESIN[20]

Acid ($1M$)	Eluant volume for peak concentration, ml	
	Uranium	Ytterbium
$HClO_4$	175	1970
HCl	78	1970
HNO_3	118	1850
H_2SO_4	40	3500
HF	7.5	Not eluted

In other work in the field of ion exchange, Korkisch[21] has recently published an extensive literature review of ion-exchange separation of uranium and thorium in mixed and nonaqueous solvents. Although this was primarily directed toward analytical applications, the information summarized may be of interest in separations process development. Solvents included alcohols, ketones, ethers, and carboxylic acids containing HCl, HBr, H_2SO_4, and other inorganic reagents.

Plant and Equipment Design and Operation

Sampling System

In any chemical process efficient sampling (either grab sampling or in-line sampling) is of prime importance to process control. In aqueous radiochemical fuel reprocessing, this is even more imperative owing to requirements of criticality and accountability control, in addition to process control. Much design and experimental effort has gone into these sampling systems over the years, and Clement and Shank[22] have recently prepared a report on a system used by Eurochemic. This system makes use of experience from French and American AEC operations as well as from work done by Eurochemic.

The report covers the background history, the present designs, and much actual experimental work on pilot models. Therefore it should serve as an excellent reference for future radioactive aqueous sampling systems or for upgrading of present systems.

Figure II-5 shows a sampling station designed for use where remote operation is required. This system makes use of "airlift" (liquid circulated by airlift effect under vacuum). The liquid is circulated through a sample bottle whose top is pierced by needles. This liquid, along with some that is bypassed, goes to an air–liquid separator, and the liquid flows by gravity back to the vessel being sampled. If in-line samples are feasible, the returning liquid from the station is run through the sensing device of the in-line instrument.

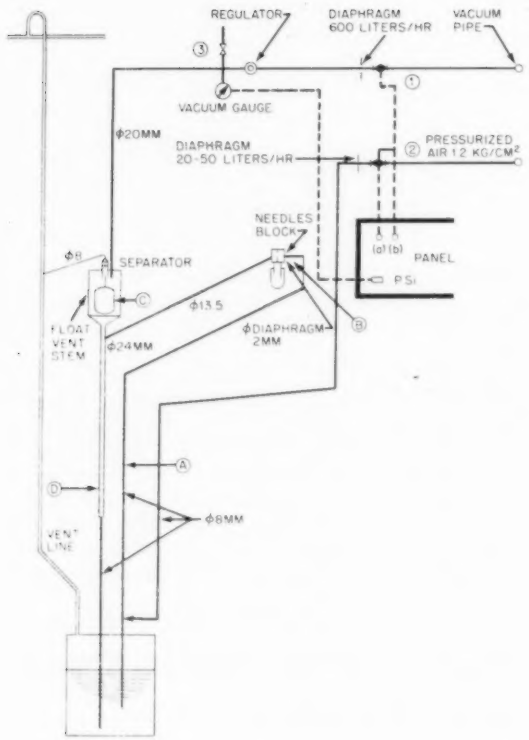


Fig. II-5. Ordinary sampling-system flow sheet.[22] Valves 1 and 2 are operated from the panel (a and b push buttons). Valve 2 will not open until valve 1 has first been opened. Furthermore, when valve 1 is shut, valve 2 is automatically closed. Diameter dimensions are internal.

In Fig. II-5 the sampling circuit is described as follows:

1. The lifting line (A) and the air-supply pipe, both 8 mm in inside diameter, are welded perpendicularly to each other. In some cases the connection is made inside the vessel to obtain higher submergences.

2. The needles block (B) is placed in the interior of a blister in the sampling corridor. It is detachable from the lifting and return pipes. The block, to which the sample bottle is attached, contains the needles and a bypass with an opening (2 mm) through which most of the flow circulates.

3. The separator pot (C) is a vessel of 2.5-liter capacity used to separate the air–liquid mixture. A float with a vacuum-relief stem constitutes the safety system against unexpected floodings.

4. The return line (D) has an inside diameter of 24 mm from the pot to approximately the middle of the total height; this avoids the formation of air bubbles and the potential airlift action. The rest is 8 mm in inside diameter.

The vacuum system, starting at the general supply, consists of the following series:

1. Automatic valve 1 interconnected with automatic air valve 2 so that the air cannot flow unless the vacuum is on.

2. A diaphragm to limit the flow.

3. A vacuum regulator—the in-series type vacuum regulator is considered preferable to the in-parallel regulator because large introduction of air into the system does not occur, one general system of vacuum only is required, and openings do not exist in the system from which contamination can spread.

4. A vacuum gauge—two set points fix the range of a signal on the panel when the vacuum corresponds to the operating zone.

5. An outlet through valve 3 for decontamination.

The air supply consists of the following, starting from the air-supply duct:

1. Regulation valve 2 mentioned above.

2. A diaphragm to allow the air flow rate to vary between 20 and 50 liters/hr, depending on the specific system.

The final safety of the system is based on good performance of the separator pot, and the following basic principles were used in its design:

1. When the pot is flooded, the upward force, resultant of the different forces acting on the float, is reasonably big and opens the relief valve to the vent.

2. The movement of the float and vent-valve system is short and well defined, giving smooth operation.

3. The relief valve is in line with the resulting upward force acting on the float.

4. The float and the relief-valve stem are separate, thus decreasing the erosion of the valve and valve seat because less weight has to be supported. At the same time this separation facilitates the operation of the valve as an overpressure relief valve.

5. Introduction of liquid in the relief-valve system is improbable during normal operation owing to (a) the separation of air and liquid in the drain line, (b) the action of the float as a screen which stops the drops, and (c) the normal exit of all flows from the pot via lines other than the relief valve.

Several possible malfunctions are discussed in detail as well as some of the experimental work involved in proving out the system experimentally.

A blister to house the sample station is shown in Fig. II-6 and is of fairly conventional design except for some of the details inside. Shielding is equivalent to 15, 10, or 0 cm of lead, depending on where it is to be used. Each blister contains the following:

1. The needle head bench with the individual needle blocks for sampling.

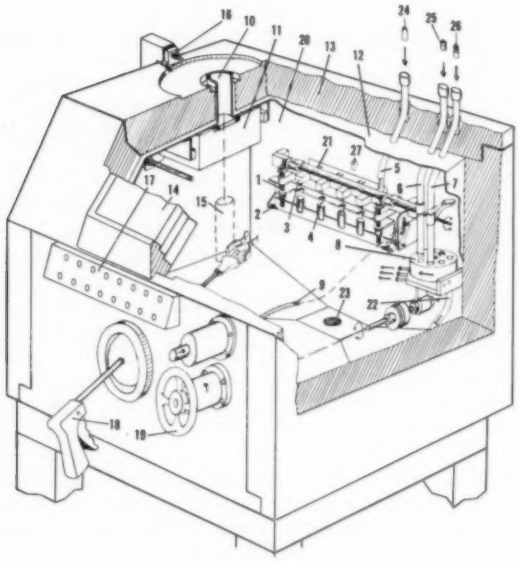
2. The cartridge closing device that is used for packing the sampling bottle into a plastic cartridge and preparing it to be sent by pneumatic post to the analytical laboratory.

3. Tongs.

4. A lead-glass window for surveying the individual operations.
5. Fluorescent lamps for lighting the sampling cells.
6. Sliding door.

The cartridge closing device produces a plastic cartridge (shown in Fig. II-7) which serves as a secondary container for the sample and as a device for pneumatic transport.

The pneumatic transporter consists of plastic lines connecting the blister to a distribution box, from



1. Needle head bench
2. Revolving transmission
3. Needles block
4. Needles
5. Connection for inserting the bottles
6. Connection for inserting the covers
7. Connection for inserting the cartridge
8. Revolving drum
9. Cartridge closing device
10. Charging door
11. Sliding door
12. Alpha box
13. Shielding
14. Lead glass window
15. Basket
16. Magnetic lock
17. Panel
18. Tongs
19. Handle for revolving drum
20. Box plate
21. Sampling loop
22. Connections to the pneumatic system
23. Drain pipe
24. Bottle
25. Cartridge covers
26. Cartridge
27. Vent line

Fig. II-6 Shielded blister.[22]

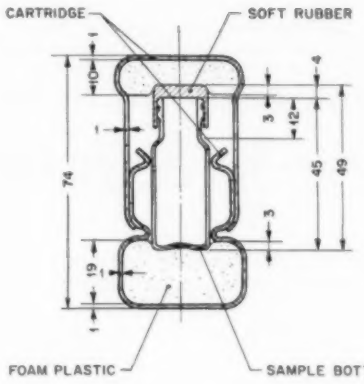


Fig. II-7 Cartridge with sample bottle.[22]

which the samples are rerouted to appropriate analytical stations.

Various safety features of the proposed system are discussed as well as the manual transport system, which can be used if the pneumatic system fails.

A great amount of discussion is included on actual experiments with the pilot models, including simulation of possible malfunctions.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

By J. J. Barghusen and W. J. Mecham

Volatility Processes for High-Enriched Fuels

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels has been successfully demonstrated at Argonne National Laboratory (ANL). A summary report has been issued describing the results of 18 runs in a pilot-scale facility that was designed to process up to 30-kg charges of uranium–zirconium alloy and 14-kg charges of uranium–aluminum alloy.[1] A description of the pilot-scale facility and the progress of engineering development work in the facility have been presented in previous issues of *Reactor Fuel Processing*.[2–4] Significant features of this report are a summary of extensive corrosion data obtained throughout the program and a detailed evaluation of the performance of various equipment components in the pilot plant.

The results of bench-scale investigations for recovering uranium from uranium–aluminum alloy fuel by fluoride-volatility methods have been recently published.[5] The report also describes the results of preliminary studies on the recovery of uranium from uranium dioxide–stainless-steel cermet fuels.

In connection with the engineering development of fluid-bed fluoride-volatility processes for enriched uranium-alloy fuels at ANL, several digital computer programs were developed to process experimental data derived in both the bench-scale and pilot-scale facilities. Descriptions of these programs are presented in a recently published report.[6]

Volatility Processes for Low-Enriched Fuels: Processing of Uranium Carbide Fuels

Several methods for treating sintered uranium carbide fuel material in preparation for uranium recovery by volatility techniques are being studied at Centre d'Etude de l'Énergie Nucléaire (CEN) at Mol, Belgium.[7] These methods involve the conversion of the carbide fuel to powdered uranium oxide or uranium fluoride, which is highly reactive toward fluorine to form UF_6. Among the agents that have been evaluated are steam or carbon dioxide for conversion to UO_2 and mixtures of oxygen and hydrogen fluoride to form UF_4 and UO_2F_2.

In tests performed with compacted uranium carbide in a fluid-bed system, it was observed that the use of water vapor (100% H_2O) at temperatures of 100 to 300°C resulted in only partial (< 50%) conversion of UC to powdered oxide. Previous work, reported in *Reactor Fuel Processing*,[8] showed that slightly higher conversion can be achieved at 500°C. Carbon dioxide at 300 to 600°C also was not effective in converting sintered UC to powdered oxide. Apparently the reaction of sintered UC with a gaseous oxidizing agent results in the formation of a protective oxide layer on the surface of the UC which precludes further reaction between UC and the oxidant.

Complete conversion of sintered UC to a mixture of UF_4 and UO_2F_2 has been achieved in a fluid-bed reactor by reaction with 47.5 vol.% HF in oxygen at 500°C. The product was a mixture of porous granules and powder.[7]

Results of preliminary experiments indicate that the fluorination of sintered UC by ClF_3 results in only partial conversion to UF_6. At 300°C approximately 80% of the UC charge was reacted in 2 hr. Complete conversion to UF_6 is not achieved owing to the formation of a protective layer on the surface of the carbide.[7]

It has been observed[9] that the reaction of UC with fluorine at temperatures between 240 and 300°C takes place in two steps. In the first step UC is rapidly converted to solid UF_4 and polymeric fluorocarbon; the latter material is found dispersed throughout the UF_4 particles. In the second step the UF_4 is converted to volatile UF_6, and the polymeric substance is fluorinated to lower fluorocarbons, primarily CF_4 and C_2F_6. The reaction during the second step follows a linear rate law at temperatures below 270°C and a parabolic rate law above 270°C. The activation energy calculated for the second step of the reaction is 22.4 kcal/mole.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

A fluid-bed fluoride-volatility process is being developed at ANL[10] to recover uranium and plutonium from spent uranium oxide fuel. In this process

the declad fuel is reacted in a fluid-bed reactor to form volatile uranium and plutonium hexafluorides, which are subsequently decontaminated and separated from one another. Of major concern in the development of the volatility process is defining the behavior of plutonium during the separation steps and establishing methods for its recovery.

FLUID-BED FLUORINATION OF UO_2 PELLETS

Fluorination of ceramic fuel to form volatile UF_6 and PuF_6 is the basis of the fluid-bed fluoride-volatility process for the recovery of uranium and plutonium from spent power-reactor fuels. A summary of engineering-scale development work at ANL on a process for the fluid-bed fluorination of UO_2 fuel pellets has been prepared by Anastasia, Gabor, and Mecham.[11] It was observed in the course of this work that the reaction between fluorine and UO_2 proceeds by a two-step mechanism: in the first step UO_2 is converted to UO_2F_2, which, in the second step, is fluorinated to UF_6. Owing to this two-step mechanism, the fluorination of a batch of UO_2 pellets proceeds through an initial induction period during which virtually no UF_6 is produced; this is followed by a period in which high rates of UF_6 production and high fluorine utilization occur. The use of oxygen rather than nitrogen as the diluent in the fluorine gas resulted in higher fluorination rates by a factor of 2 or 3. Oxygen apparently enhances fluorination by the formation of U_3O_8, which spalls off the pellet surface and mixes in the fluid bed as reactive fines of high specific surface area. The formation of highly reactive U_3O_8 by oxidation of sintered UO_2 pellets is now being used as the basis of a method for fluorinating UO_2 fuel. In this method, called two-zone oxidation–fluorination, oxidation of the pellet fuel occurs in the lower section (oxidation zone) of the fluid bed in which UO_2 pellets are mixed with alumina particles. The U_3O_8 fines formed in the oxidation zone are transported by the fluidizing gas to the upper section (fluorination zone) of the fluid bed which contains alumina only. Here the fines are fluorinated in a fluorine gas stream introduced into the reactor at a point just above the oxidation zone. In the two-zone system, the less exothermic oxidation reaction occurs in the fluidized packed bed of sintered pellets, and the highly exothermic fluorination reaction occurs in the upper fluid-bed section where heat-transfer coefficients are significantly higher than in the fluidized-packed-bed section. Uranium hexafluoride production rates of 50 lb/(hr)(sq ft) and fluorine utilization efficiencies of 75% have been achieved in a 3-in.-diameter fluid-bed reactor by the use of the two-zone fluorination technique.

In one concept of the fluid-bed fluoride-volatility process for UO_2 fuel, the oxide fuel is converted completely to U_3O_8 powder prior to fluorination. One of the aspects of the oxidative pulverization of UO_2 pellets that has been studied is the distribution of the U_3O_8 in the fluid bed after oxidation.[12] This distribution, which is important in the assessment of sampling procedures for uranium and plutonium, was studied with UO_2 pellets that contained ^{235}U in concentrations approximating the plutonium concentrations expected in UO_2-PuO_2 fuels. It was assumed that the distribution behavior of ^{235}U and plutonium are both the same during oxidation of the fuel. In these tests 6-in.-deep beds of UO_2 pellets consisting of equal quantities of depleted (0.2198% ^{235}U) and normal (0.7218% ^{235}U) UO_2 pellets were charged to a 3-in.-diameter fluid-bed reactor and oxidized at 450°C with 19 vol.% oxygen in nitrogen. Bed samples taken after 5.5 hr of oxidation from sampling points 8, 28, and 38 in. above the bottom of the fluid bed contained 0.4645, 0.4650, and 0.4714% ^{235}U, respectively, in the uranium, thus indicating that the uranium content of the sample is homogeneous with respect to ^{235}U. The concentration of uranium in the bed samples varied slightly with bed elevation; the sample from the lower portion of the bed contained 28.3 wt.% uranium, and the sample from the upper portion of the bed contained 32.3 wt.% uranium.

The direct fluorination of large quantities of uranium oxide fines within a fluid bed requires careful control to avoid local regions of high temperatures which may bring about the sintering of particles in the bed. An analysis of the data from experiments performed at ANL[13] involving the fluorination of uranium oxide fines suggests that the formation of a cake within the fluid bed (sintering of particles to form an agglomerate) might result from a combination of high temperature in the fluid bed, low gas velocity in the bed, and low concentrations of fluorine in the off-gas stream. An excess of fluorine in the off-gas can be provided by reducing the fluorine utilization through a reduction in the fluorination temperature or through an increase in gas velocity. These conditions were successfully applied in a test that involved the fluorination of 2.3 kg of uranium oxide fines in a 3-in.-diameter fluid-bed reactor. Approximately 2.9 kg of alumina was used as the inert fluid-bed material. The fluorination was carried out at 350°C with 12 vol.% fluorine in nitrogen as the fluidizing gas. The superficial gas velocity in the fluid-bed reactor was 1.5 ft/sec. The fluorination was completed in 2.5 hr, during which the UF_6 production rates averaged 50 lb/(hr)(sq ft). The alumina bed material at the end of the run was free flowing.

FLUID-BED FLUORINATION OF UO_2-PuO_2 PELLETS

Jarry et al.[14] have summarized the results of laboratory-scale investigations of the fluid-bed fluorination of simulated oxidic nuclear fuels containing plutonium. The purpose of the investigations was to determine the best reaction conditions for the fluorination of uranium and plutonium from simulated fuel mixtures containing U_3O_8, PuO_2, nonradioactive

fission-product oxides, and alumina fluid-bed material. The progress of the investigations has been reported in previous issues of *Reactor Fuel Processing*.[15–17] The significant findings of these studies were that more than 99% of the uranium could be removed from the alumina bed by reaction with fluorine at temperatures of 450 to 500°C, whereas an additional 10 hr at 550°C was required for the removal of 96 to 98% of the plutonium. Plutonium recoveries of greater than 99% were achieved by reuse of the alumina bed for the fluorination of additional fuel material. Plutonium retention on the alumina bed was not affected by the type of alumina used as bed material (sintered or fused granules), the particle size range of the alumina, or by the presence of stainless-steel decladding products resulting from oxidation of stainless steel by mixtures of HF and oxygen. Plutonium retention on the alumina was influenced by the flow rate of the fluorinating gas and by the quantity of fission products and plutonium charged to the reactor.

These studies have been extended to demonstrate the recovery of uranium and plutonium from UO_2–PuO_2 pellets by fluorination in a 2-in.-diameter fluid-bed reactor.[10] The pellets used in this study contained 0.4 wt.% plutonium (as PuO_2), 86 wt.% uranium (as UO_2), and 1 wt.% nonradioactive fission products (as the oxides). Fluorination of the pellets was carried out as follows: a 2-in.-deep fluidized packed bed of UO_2–PuO_2–fission-product pellets (650 g of pellets and 1100 g of alumina) was fluorinated according to the sequence (1) a two-zone oxidation–fluorination step for 3 hr at 450°C, (2) a once-through fluorination step for 1 hr at 450°C with 10 vol.% fluorine, and (3) a recycle fluorination step with 90 vol.% fluorine for 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C. These conditions resulted in final uranium and plutonium concentrations in the alumina bed of 0.004 and 0.007 wt.%, respectively. These values are equivalent to uranium and plutonium removals of greater than 99.9% and 97% for a single use of the alumina bed. Recent results[18] have shown that the overall recycle fluorination time can be reduced from 20 to 12 hr without affecting the final plutonium retention on the alumina.

In tests in which 0.6 g of CsF was added to the alumina bed to simulate more closely the conditions that might exist in the reprocessing of irradiated fuel, the residual concentration of both uranium and plutonium in the final bed was slightly higher than in the absence of cesium.[19,20] A modified fluorination procedure was developed to improve removals of plutonium from beds of alumina containing cesium. Results from preliminary experiments[20] indicate that the concentration of plutonium on the alumina can be reduced to a satisfactory level (0.009 wt.%) for a single use of the alumina bed by a two-step fluorination procedure. In these experiments UO_2–PuO_2–fission-product pellets were reacted in the following manner in an alumina fluid bed containing CsF: (1) the pellets were pulverized by oxidation with 20 vol.% oxygen for 3 hr at 450°C and (2) the uranium and plutonium oxides were fluorinated with 10 vol.% fluorine for 2.5 hr at 300°C and for 3 hr at 350°C, and the residue was subjected to recycle fluorination with 90 vol.% fluorine for 3 hr at 350°C, for 6 hr while the bed temperature was increased from 350 to 550°C in increments of 5°C every 9 min, and finally for 3 hr at 550°C.

OPERATIONS FOR THE SEPARATION OF URANIUM FROM PLUTONIUM

Of major concern in the development of fluoride-volatility processes for low-enriched UO_2 fuel is the establishment of methods for the separation of uranium from plutonium and for the recovery of plutonium. A method for effecting the separation of uranium from plutonium based on the selective fluorination of uranium from UO_2–PuO_2 fuel by chlorine trifluoride is being developed at CEN.[7] Plutonium is recovered as PuF_6 in a subsequent step by fluorination with fluorine.

A series of engineering-scale tests has been performed[7] to evaluate the direct fluorination of sintered UO_2 pellets with ClF_3. The tests were carried out in a vertical tube 3.4 cm in diameter with 500-g batches of UO_2 pellets containing 0 to 5 wt.% synthetic fission products. At 100°C the presence of fission products results in a decrease in the reaction rate proportional to the quantity of fission products in the oxide. At 300°C an entirely different effect was observed wherein a slightly higher reaction rate occurred at intermediate concentrations of fission products.

The presence of 200 g of alumina particles (diameter, 100 to 200 μ) apparently decreases the rate of reaction between sintered UO_2 and ClF_3 at 100 and 300°C.

A packed bed of sodium fluoride pellets was employed in these tests to collect the gaseous reaction products. Complete sorption of UF_6 on the NaF pellets was obtained. The volatile fission-product species were molybdenum at reaction temperatures of 100 and 300°C and niobium and ruthenium at 300°C.

Workers at ANL are investigating a method for effecting the separation of uranium from plutonium based on the selective fluorination of uranium with bromine pentafluoride. Since BrF_5 converts uranium compounds to volatile UF_6 and plutonium compounds to nonvolatile PuF_4, a separation between uranium and plutonium can be achieved. Results of studies of the kinetics of reactions between various uranium compounds and BrF_5 have been reported in previous issues of *Reactor Fuel Processing*.[21,22] Recent work at ANL[23] has shown that, in the reactions between BrF_5 and UF_4 and between BrF_5 and U_3O_8, BrF_5 is completely reduced to bromine rather than to BrF_3. Bromine could result from either the direct reduction of BrF_5 or from a two-step process involving the formation of a BrF_3 intermediate compound. The

rate of reaction of UF_4 with BrF_3 is approximately 5 to 10 times the rate of reaction of BrF_5 with UF_4, and thus, if BrF_3 is formed as an intermediate compound, the reduction of BrF_3 to bromine would not be the rate-controlling step.

The use of BrF_5 as a selective fluorinating agent is being evaluated with sintered UO_2-PuO_2–fission-product pellets in a 2-in.-diameter fluid-bed reactor.[19,20] Demonstration tests have been performed with the use of 650 g of oxide pellets in 1100 g of alumina fluid-bed material. Since the direct reaction of sintered oxide fuel does not occur readily with BrF_5 alone or in mixtures with oxygen at temperatures up to 400°C, the oxide fuel is pulverized to $U_3O_8-PuO_2$ powder by reaction with oxygen prior to fluorination. In these tests oxidation was carried out for 4 hr at 450°C with 20 vol.% oxygen in nitrogen. The uranium was converted to UF_6 by reaction with 11 vol.% BrF_5 in nitrogen for 1.8 hr at 300°C. The recycle fluorination step with fluorine for the volatilization of plutonium was carried out as follows: 1 hr at 300°C while the fluorine concentration was increased from 10 to 90 vol.%; 2 hr at 300°C with 90 vol.% fluorine; 5 hr with 90 vol.% fluorine while the bed temperature was increased from 300 to 550°C in increments of 10°C every 12 min; and 2 hr at 550°C with 90 vol.% fluorine.

Approximately 99% of the uranium was converted to UF_6 during the 1.8-hr fluorination period with BrF_5. The removal of plutonium was satisfactory, the residual plutonium concentration in the final alumina bed being 0.007 wt.%. Tests have shown that the presence of cesium in the alumina fluid bed does not affect the extent of plutonium removal during recycle fluorination.[20]

Preparation and Properties of Fluorides

PROPERTIES OF URANIUM HEXAFLUORIDE

Decontamination of UF_6 produced by fluoride-volatility techniques can be accomplished by an absorption–desorption cycle in a bed of NaF pellets. Uranium hexafluoride interacts with sodium fluoride to form either $UF_6 \cdot 2NaF$ or $UF_6 \cdot NaF$ depending on the partial pressure of UF_6 and the temperature. Katz[24] has recently described the preparation and properties of $UF_6 \cdot NaF$ and homologous compounds prepared from WF_6 and MoF_6. Equations describing the effect of temperature on the dissociation pressures of these compounds were presented in the previous issue of *Reactor Fuel Processing*.[25]

Oak Ridge National Laboratory (ORNL)[26,27] workers have shown that sorption–desorption techniques used with NaF beds are effective in removing volatile chromium fluorides from UF_6. Chromium fluorides are present in the fuel salt for the Molten Salt Reactor Experiment as a result of corrosion of the reactor piping and of the equipment used for hydrofluorinating and fluorinating the salt during reprocessing. In the fluorination step of the reprocessing operation, volatile chromium fluorides (CrF_4 and CrF_5) appear with UF_6 in the fluorinator off-gas. Tests[26] have shown that fixed beds of NaF pellets at 400°C are effective in removing chromium fluorides from a gas stream that also contains UF_6 and fluorine. Pelleted NaF having a surface area of 0.074 m^2/g and a void fraction of 0.277 was found to be superior to material with a surface area of 1 m^2/g and a void fraction of 0.45. The effective capacity of pelleted NaF is about 20 g of chromium per 100 g of NaF. Uranium losses of less than 0.01% were achieved in tests using fluorine gas streams containing 0.4 mole of chromium fluoride per mole of UF_6.

Chromium fluorides also are produced during the processing of stainless-steel-clad fuel material. Stainless-steel fuel is first declad by destructive oxidation with HF–oxygen mixtures. During fluorination volatile chromyl fluoride (CrO_2F_2) is produced; it is conveyed from the fluorinator in the UF_6 product gas stream. The dissociation pressure for the $NaF-CrO_2F_2$ complex can be expressed by the relation $\log P\,(\text{mm Hg}) = -0.865 - 579/T$. When this expression is compared with that relating the dissociation pressure of UF_6 over $2NaF \cdot UF_6$ [$\log P\,(\text{mm Hg}) = 10.88 - 5090/T$], it appears that at temperatures above 400°K the UF_6 pressure is more than 10 times that of CrO_2F_2, and UF_6 may be desorbed from NaF using the usual purification procedures (desorption at 573°K) without significant contamination by chromium.[27]

Moncelon, Lucas, and Kikindai[28] have investigated the reaction between SO_2 and UF_6 and have observed that the nature of the uranium fluoride product was highly dependent on the partial pressures of the reactants and the reaction temperature. The uranium fluorides identified as reaction products were αUF_5, βUF_5, U_2F_9, and UF_4. For a mole ratio of SO_2/UF_6 of 5, αUF_5 was the only solid fluoride product at 150 and 270°C; at 370°C the product was a mixture of αUF_5 and U_2F_9. For an equal molar mixture of SO_2 and UF_6, a mixture of UF_4 and U_2F_9 was produced at 374°C. The reaction appeared to follow second-order kinetics with an SO_2/UF_6 mole ratio of about 2.

FLUORIDE COMPLEXES OF PLUTONIUM AND PROTACTINIUM

Penneman and associates at Los Alamos Scientific Laboratory have observed[29] that, when an intimate mixture of PuF_4 and RbF is fluorinated with 1 to 115 atm of fluorine for 4 to 16 hr at 300 to 400°C, a green salt, Rb_2PuF_7, containing pentavalent plutonium is produced. The X-ray powder pattern of this material was indexed as monoclinic, and therefore the material is isostructural with Rb_2UF_7, which is a compound of pentavalent uranium. When cesium plutonium(IV) fluoride (1:1 mole ratio Cs:Pu) was fluorinated at 350°C, $CsPuF_6$ containing pentavalent plutonium was produced. This material was iso-

structural with rhombohedral $CsUF_6$. The compound had a unique absorption spectrum unlike that of Pu(III), Pu(IV), or Pu(VI). The pentavalent-plutonium complex gradually altered after several days, forming $CsPuF_5$. Titration of iodine liberated by a freshly prepared sample of $CsPuF_6$ showed that more than 90% of the plutonium was in the pentavalent state.

Workers at ORNL[27] have observed that when PuF_6 gas is contacted with sodium fluoride at 600°C the product is a green solid, Na_3PuF_7, which has a diffraction pattern nearly identical to that of Na_3UF_7. This material did not release any iodine. The product from the reaction between PuF_6 and NaF at 100°C released iodine in an amount equivalent to a plutonium oxidation number of about 4.75.

Pentavalent protactinium forms a variety of complex fluorides with alkali fluorides. These complexes may be prepared either from aqueous hydrofluoric acid solutions or by fluorine oxidation of intimately ground stoichiometric mixtures of PaF_4 and alkali fluoride. Asprey et al.[30] have prepared and characterized complexes of the type $MPaF_6$ where M is Li, Na, K, Rb, Cs, and NH_4. The crystalline $MPaF_6$ compounds containing the larger cations (K^-, Rb, Cs, and NH_4) are orthorhombic, whereas $NaPaF_6$ is tetragonal. The lithium complex was not characterized. In other work Brown and Easey[31] prepared from aqueous hydrofluoric acid solutions anhydrous heptafluoroprotactinates(V), M_2PaF_7, where M is K, NH_4, Rb, and Cs. Using aqueous solutions, they also prepared lithium and sodium octafluoroprotactinates(V). The octafluoro complexes of potassium and cesium, K_3PaF_8 and Cs_3PaF_8, were prepared by heating the alkali-metal fluoride and the heptafluoro complex in an inert atmosphere. A survey of recent work on the fluoro complexes of protactinium has been published.[32]

CHLORINE FLUORIDES

Chlorine trifluoride is currently being used for the production of UF_6 from uranium compounds and also is being considered as a fluorinating agent in the reprocessing of reactor fuel materials by fluoride-volatility techniques. The interaction of ClF_3 with various materials and chemical compounds is therefore of general interest.

Workers at the Paducah Gaseous Diffusion Plant[33,34] have investigated the gas-phase reaction between ClF_3 and water. The reaction of ClF_3 and H_2O at 25°C was studied to determine the nature of the reaction products.[33] It was found that with excess ClF_3 present the products were chiefly HF, ClF, and ClO_2F. With excess water present the products were mainly HF, O_2, and Cl_2. It was suggested that successive reactions occur:

$$2ClF_3 + 2H_2O \rightarrow 4HF + ClF + ClO_2F$$

$$2ClF + H_2O \rightarrow 2HF + Cl_2 + 0.5\ O_2$$

$$2ClO_2F + H_2O \rightarrow 2HF + Cl_2 + 2.5\ O_2$$

The complete reaction at 25°C would then be represented as

$$2ClF_3 + 3H_2O \rightarrow 6HF + Cl_2 + 1.5\ O_2$$

However, these equations do not completely describe the reaction since small quantities of ClO_3F were usually present.

At 93°C the ClF_3-H_2O reaction produces the same species as at 25°C; the primary reaction produces ClF, ClO_2F, and HF, with oxygen and chlorine derived from secondary reactions.[34]

Preliminary results of an investigation of the $ClF-H_2O$ reaction suggest that the products of the reaction are O_2, Cl_2, ClO_2F, Cl_2O, and HF in amounts that appear to depend on the relative amounts of the reactants.[34]

Chlorine pentafluoride has been prepared[35] by the reaction between fluorine and chlorine trifluoride at 30°C. The product is a colorless gas that does not tend to decompose at room temperature. The vapor pressure of liquid ClF_5 can be represented by the equation $\log P\ (\text{mm Hg}) = 7.71 - 1257/T$. The heat of vaporization at the boiling point (−12.9°C) is 5.74 kcal. In the gas phase ClF_5 is monomeric. Chlorine pentafluoride dissolves rapidly in a 0.5% solution of sodium hydroxide.

Volatility Processing of Fuel and Blanket of a Molten-Salt Thermal Breeder Reactor

A preliminary design and an engineering evaluation and cost study[36] were made at ORNL of a plant for treating the fuel and blanket streams of a 1000-Mw(e) molten-salt thermal breeder reactor. The plant was designed to operate continuously as an integrated part of the reactor system and to take full advantage of shared costs of the combined system. The plant capacity is based on the treatment of 15 cu ft of fuel salt per day and 105 cu ft of blanket salt per day, both removed as side streams from the reactor. The primary requirements of the process are to recover (1) the unburned fuel ($^{233}UF_4$) and fuel-stream carrier salt ($LiF-BeF_2$) from the fuel stream and (2) the $LiF-ThF_4$ salt and the bred ^{233}U from the blanket stream. Both streams must be sufficiently decontaminated for attractive breeding performance of the reactor. Facilities are provided for underground storage of radioactive wastes as solids in tanks located on the processing site.

The processing steps are nonaqueous throughout. Fluoride-volatility techniques are used to separate and decontaminate uranium, and vacuum distillation is used to decontaminate the fuel-stream carrier salt. Salt distillation and continuous fluorination are the principal process steps that differ from earlier conceptual designs for processing molten-salt breeder reactor fuel. These earlier processes were reviewed in the Spring 1965 and Fall 1965 issues of *Reactor Fuel Processing*.[37,38] An earlier plant concept and a

cost estimate for a fused-salt fluoride-volatility plant were described in the Fall 1963 issue of *Reactor Fuel Processing*.[39]

The major steps in the present conceptual process are shown in Fig. III-1. As shown in the figure, the fuel salt stream is purified by fluorination and vacuum distillation. The first step removes uranium as volatile UF_6 from the fuel salt by sparging the molten salt with fluorine; the second step recovers the $LiF-BeF_2$ by simultaneously volatilizing these two components from the less volatile fission products. The less volatile fission products so separated are primarily the rare earths, which are the most serious neutron poisons. The UF_6 from the fluorinator is accompanied by some volatile fission-product fluorides, primarily those of the elements molybdenum, tellurium, ruthenium, zirconium, and niobium, which are removed by sorption on granular NaF and MgF_2. Finally, the UF_6 is reduced to UF_4 by hydrogen and recombined with the decontaminated $LiF-BeF_2$ carrier salt in a single operation in which UF_6 and hydrogen are introduced into the molten salt as sparge gases. The bulk of the fission-product waste is discarded in the NaF and MgF_2 sorbents and in the still residues, which are highly concentrated solutions of the rare earths in LiF.

The blanket salt stream is processed by fluorination followed by decontamination of the UF_6 on NaF and MgF_2 sorbents, in a manner similar to that used for the fuel salt. The bred ^{233}U is removed at a rate sufficient to maintain a low concentration in the blanket. As a result, fissioning of ^{233}U and poisoning by fission products are negligible. Discard of the barren salt from the blanket salt stream at a low rate suffices to keep the fission-product concentration in the blanket stream at a tolerable level.

The major items of molten-salt processing equipment are the continuous fluorinator, the continuous-reduction column, and the salt-distillation unit; the conceptual designs of these equipment items are shown in Figs. III-2, III-3, and III-4, respectively. Equipment associated with the volatile UF_6 stream is similar to that employed in the ORNL fused-salt fluoride-volatility pilot plant, which has been extensively described in previous issues of *Reactor Fuel Processing*.[40–43]

Corrosion in a molten-salt environment is an area where further information is needed for evaluation of the plant design. Alloys specified in the report for fused-salt processing equipment were INOR-8 (16% molybdenum, 5% iron, 7% chromium, 71% nickel) and alloy 79-4 (4% molybdenum, 16% iron, 79% nickel).

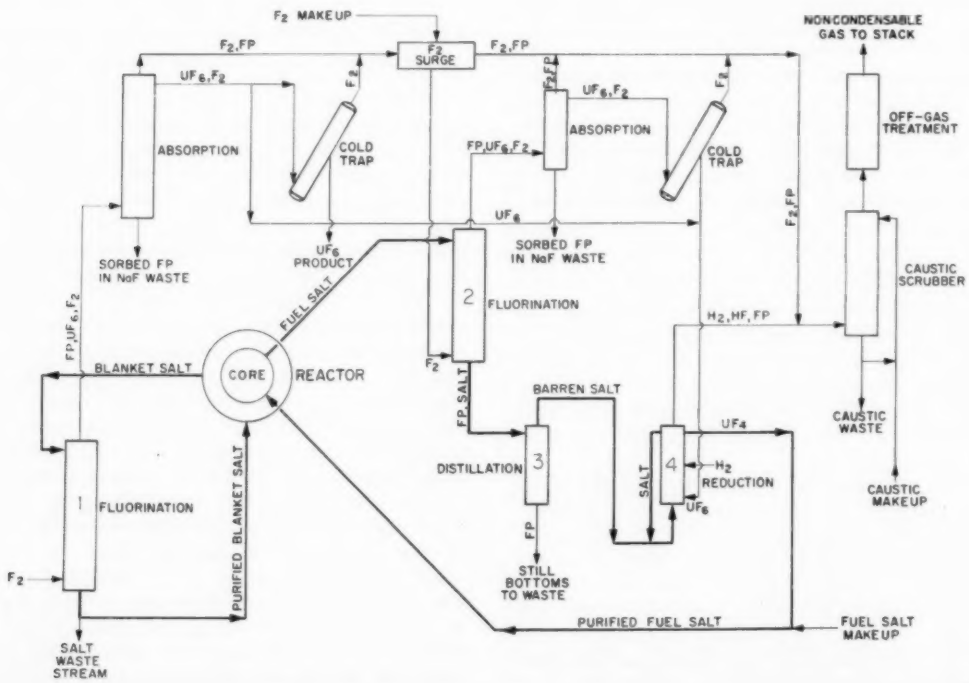

Fig. III-1 Major steps in molten-salt breeder reactor fuel and blanket processing.[36] Uranium is separated from blanket and fuel salts by fluorination (blocks 1 and 2), further purified by sorption, and collected in cold traps. The barren fuel-carrier salt is distilled away from the bulk of the fission products (block 3). The cold-trapped UF_6 and fuel-carrier salt are recombined in the reduction step (block 4) and returned to the core.

Extensive corrosion tests have been made on these alloys in connection with the ORNL fused-salt fluoride-volatility process development. A frozen-wall technique is specified for use in the fluorinator to minimize contact of the metal with the molten salt. (A study of the frozen-wall technique at ANL was reviewed previously in *Reactor Fuel Processing*.[43])

Heat removal is a major problem in all process vessels that contain short-cooled, highly irradiated fuel. A sodium–potassium eutectic mixture (NaK) was chosen as the primary coolant for process vessels at temperatures above 500°C and where large amounts of heat must be removed. The NaK circulation system also has the capability of heating the system to 600°C for startup. Air was chosen as the coolant for low heat fluxes.

The system was designed for a campaign type operation of one-month duration, without shutdown except for emergency maintenance. There is no access to the operating areas during this period. At the end of the operating period, the entire system is closed down, routine maintenance is accomplished, feed hoppers are replenished, accumulated waste is transferred to waste storage, and other preparations are made for the next cycle of operations.

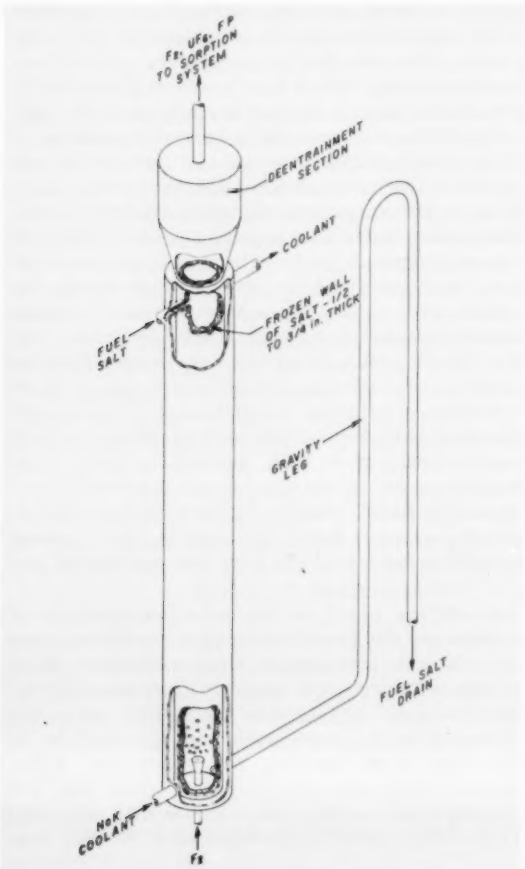

Fig. III-2 Continuous fluorinator.[36] NaK coolant, flowing through the jacket, freezes a layer of salt on the inner surface of the column, thus protecting the alloy 79-4 from corrosive attack by the molten-salt–fluorine mixture.

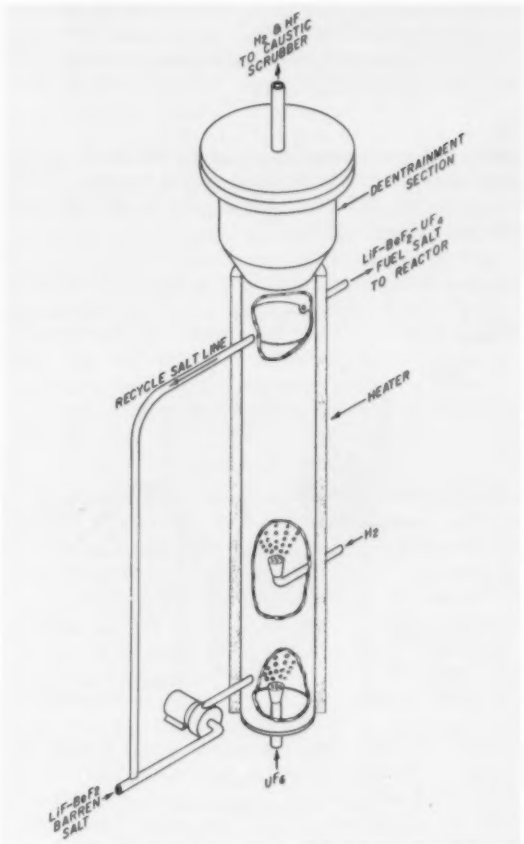

Fig. III-3 Continuous-reduction column.[36] Barren salt and UF_6 enter the bottom of the column, which contains circulating $LiF-BeF_2-UF_4$. The UF_6 dissolves in the salt, aided by the presence of UF_4, and moves up the column, where it is reduced by hydrogen. Reconstituted fuel is taken off the top of the column and sent to the reactor core. INOR-8 is the specified construction material.

Maintenance of high-level-activity process vessels entails decontamination in a separate facility before repair. Low-level-activity vessels are directly maintained after decontamination by means of a molten-salt flush and an aqueous wash.

The estimate of incremental capital costs for the processing and waste-storage facility was $2,600,000 for the building and equipment and $5,500,000 for the total fixed investment.

The estimated annual fuel-processing charge was as follows:

Direct operating cost	$ 610,190
Labor overhead (80% labor cost)	177,600
Fixed costs	
Depreciation (10% of fixed capital per year)	549,820
Tax (1% of fixed capital)	54,980
Insurance (1% of fixed capital)	54,980
Total	$1,447,570

The total processing charge of $1,450,000 is equivalent to about 0.20 mill/kw(e)-hr for reactor operation with an 80% plant factor and a 45% thermal efficiency.

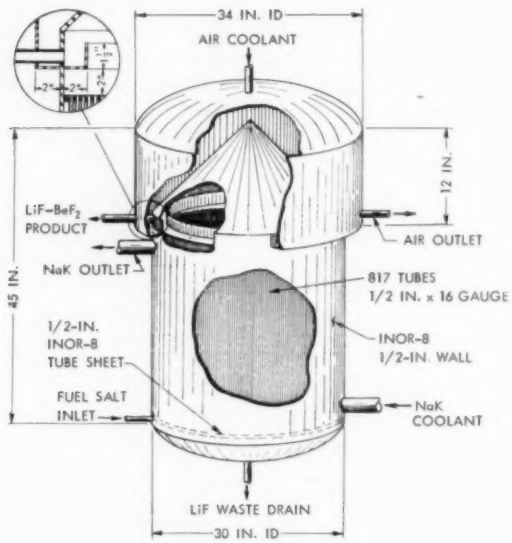

Fig. III-4 Vacuum still for molten-salt breeder reactor fuel.[36] Barren fuel-carrier flows continuously into the still, which is held at about 1000°C and 1 mm Hg. The LiF–BeF_2 distillate is removed at the same rate that salt enters, thus keeping the volume constant. Most of the fission products accumulate in the still bottoms. The contents are drained to waste storage when the heat-generation rate reaches a prescribed limit. This concept of the vacuum still has not been tested.

Compact Pyrochemical Processes

By L. Burris and G. A. Bennett

Compact pyrochemical processes are nonaqueous processes for the recovery and purification of partially burned reactor fuels. They possess utility for the recovery of ceramic fuels (such as oxides or carbides) as well as metallic fuels and may be used in small plants serving one or several reactors. In general, these processes utilize molten-metal and molten-salt systems as processing media. The metal solvent systems consist principally of various binary alloys of magnesium with zinc, cadmium, and copper. Systems employing ternary alloys are also being studied. The salt systems are halide salts of alkali and alkaline-earth metals. It is also possible to process both ceramic and metallic fuels directly, i.e., without dissolution in any solvent media.

These processes possess features that should be economically beneficial, particularly in fast reactor fuel cycles. Among these features are (1) the ability to process short-cooled high-burnup fuels, both ceramic and metallic, with consequent reductions in fuel inventory, (2) the decrease in criticality problems because of the absence of aqueous solutions, (3) the recovery of expensive alloying agents, and (4) the direct production of concentrated fission-product wastes.

Processes for Future Fast Reactor Fuels

SALT-TRANSPORT PROCESSES

Salt-transport processes, currently under development at ANL,[44–46] are processes in which the fissile and fertile constituents of the fuel are selectively transferred from one liquid-metal solvent to another by cycling a molten-salt phase between the two metal solvents. The selective transport of the valuable fuel constituents takes place as a result of differences in distribution coefficients and solubilities of the fuel constituents in the two metal/salt solvent systems.

The concept of fuel purification by transport through salt offers the inherent advantage over other pyrochemical processes that only small solution volumes are required since only a small fraction of the uranium or plutonium needs to be in solution at any one time. Because process volumes are small, the process may be readily adapted for use in small, compact reprocessing plants. These processes also offer the possibility of excellent separation of fission products from uranium and plutonium and excellent recoveries of uranium and plutonium. To date, both laboratory- and engineering-scale investigations have been carried out at ANL, and data on distribution coefficients, solubilities, and separation factors have been accumulated. The Spring 1966 issue of *Reactor Fuel Processing*[44] listed the various alloy systems under consideration and gave the advantages and disadvantages of each.

A process based on the selective transport of uranium and plutonium from a copper–magnesium solvent alloy to appropriate zinc–magnesium alloys through a chloride salt phase is currently under investigation at ANL. A conceptual flow sheet was presented in the above mentioned Review.[44] In the first step of this process, fuel oxides (e.g., a discharged mixed uranium–plutonium oxide fuel) are suspended in a molten salt, which is then vigorously mixed with a liquid-magnesium alloy. By this procedure the uranium and plutonium oxides (together with the fission-product oxides) are reduced to the metal. The undissolved fraction of the reduced uranium and plutonium is preferentially wetted by the liquid-metal-alloy phase, and therefore is present in

this phase as a precipitate. Since the molten salt is a waste stream, it is desirable to achieve complete oxide reduction and to minimize the concentrations of dissolved uranium and plutonium. These two requirements depend on the magnesium chloride concentration of the molten salt in opposite ways: a high $MgCl_2$ concentration favors rapid oxide reduction, whereas a low $MgCl_2$ concentration is required to minimize the concentrations of dissolved uranium and plutonium compounds. Therefore it is necessary to optimize this process step with respect to these conflicting requirements. At the same time it is desirable that the rare earths distribute as strongly as possible into the salt phase so that they can be separated from uranium and plutonium and be discarded in the waste salt.

One aspect of this problem was investigated in the laboratory by measuring the dependence of the concentration of uranium and cerium (a representative rare-earth element) in a $CaCl_2-NaCl-MgCl_2$ salt mixture on the $MgCl_2$ concentration when in equilibrium with a liquid copper–magnesium alloy at 800°C. These measurements indicated the following:[47] (1) at a constant metal-phase composition, the concentrations of UCl_3 and $CeCl_3$ in the molten salt may vary by several orders of magnitude as the concentration of $MgCl_2$ is varied from about 1 to 60 mole %, (2) the distribution coefficient* is proportional to the three-halves power of the $MgCl_2$ concentration, and (3) the ratio of uranium to cerium in the salt phase is approximately independent of the $MgCl_2$ concentration of the salt. Thus the separation factor (distribution coefficient of cerium/distribution coefficient of uranium) and therefore the required number of separation stages are essentially independent of the $MgCl_2$ concentration.

In addition to copper–magnesium, two ternary alloys are being considered for possible use in the salt-transport process: (1) cadmium–copper–magnesium alloy[45] and (2) cadmium–zinc–magnesium alloy.[45–47] These alloys offer the possibility of lowering the operating temperature to about 600°C (800°C is the required operating temperature with the copper–magnesium alloy) and may permit the use of a wider variety of construction materials.

In engineering work related to salt-transport processes, information was obtained on the effect of mixing speed on the entrainment of the metal phase in the salt phase.[47] These data will be useful for designing continuous, differential type extraction equipment, such as a circulating-salt loop system.

Materials Evaluation

A supporting program is under way at ANL to find inexpensive, easily fabricated materials for these salt-transport processes. Various ferrous alloys are currently under test. Among the more promising is type 405 stainless steel, which is suitable for use with cadmium-based systems containing low percentages of uranium.[45] In a recent experiment[45] the stability of a 0.45 wt.% solution of uranium in cadmium–3.7 wt.% magnesium alloy on long-term (169-hr) exposure at 425°C to type 405 stainless steel was determined. (A 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl molten-salt phase was also present in the experiment.) After an initial loss of 3.2% of the uranium from the liquid-metal solution, no further uranium loss occurred during the remainder of the 169-hr test period. Thus it appears that type 405 stainless steel may be a satisfactory container material for this system after it has undergone an initial conditioning exposure to the solutions.

Equipment Development

A number of equipment components, such as valves, pumps, flowmeters, liquid-level detectors, and pressure-measuring devices, are required for processes employing liquid-metal and liquid-salt systems. Investigators at ANL have assembled a test loop for the testing of such equipment.[48] A centrifugal pump, an orifice flowmeter, two types of pressure sensors, a freeze valve, and a bellows-sealed throttling valve were installed in the loop for performance evaluation. The loop was operated for 60 hr during which liquid 50 mole % $MgCl_2$–30 mole % NaCl–20 mole % KCl at 500°C was circulated at an average flow rate of 0.9 gal/min. Operation of the loop was satisfactory. The freeze valve was opened and closed six times without difficulty to permit filling and emptying of the loop. Following this initial operating period, the loop was shut down for minor modifications in the auxiliary equipment. When these modifications have been completed, the loop will again be placed in operation.[47]

CONVERSION OF FLUORIDES TO OXIDES IN FUSED-SALT MEDIA

Additional progress is reported[7] by investigators at Centre d'Étude de l'Énergie Nucléaire (CEN), Mol, Belgium on the conversion of fluorides to oxides in fused-salt media. In this process fluorides of uranium or plutonium (UF_4, UF_6, PuF_4, PuF_6) are dissolved in a molten-chloride-salt mixture, such as the LiCl–KCl eutectic. The salt is then sparged with an oxygen-containing gas (such as an oxygen–HCl mixture). This results in the precipitation of plutonium as PuO_2; the uranium remains in solution as uranyl ion. The uranium can be removed in a later step by electrodeposition of UO_2 on a graphite cathode or by chemical precipitation of UO_2 by hydrogen sparging.

In the latest investigations the oxidation time was reduced by using a mixture of lithium and potassium nitrates (in proper proportion so that the eutectic

*Distribution coefficient (k_d)

$$= \frac{\text{wt.\% of transferring element in salt}}{\text{wt.\% of transferring element in metal}}$$

LiCl–KCl ratio does not change) instead of an oxygen–HCl mixture. This reaction is immediate, precipitating PuO_2 and forming soluble UO_2F_2 from the respective tetrafluorides. The reaction is carried out in a pyrex cell at 500°C. Impurities are kept low by dehydration (with HCl gas) before electrolysis.

The PuO_2 obtained by reaction with KNO_3 from the oxidation of mixed uranium and plutonium fluorides (2.5 g of UF_4, 300 mg of PuF_4) appears to contain more LiF than PuO_2 precipitated by reacting with a mixture of oxygen and chlorine. This impurity can be eliminated by washing with 2*M* HNO_3 for a sufficient period of time; however, such washing can dissolve 10 to 12% of the plutonium.

Processes for Current Reactor Fuels

EBR-II SKULL-RECLAMATION PROCESS

After fuel pins discharged from the Experimental Breeder Reactor No. 2 in Idaho have been melt refined,[49] a uranium-bearing residue, or skull, is left in the crucible. The uranium in this skull amounts to 5 to 10% of the original uranium charge. A process known as the skull-reclamation process is being developed by ANL for the recovery and purification of the uranium in this skull. The chemistry and technology that are being accumulated in the course of this process development have considerable potential utility for plutonium–uranium oxide and carbide fuels.

Currently the skull-reclamation process is being demonstrated with unirradiated materials in remotely operated plant-scale equipment (~4 kg of uranium per batch) comprised of a reduction furnace and a retorting furnace. The process, details of which have been reported in previous issues of *Reactor Fuel Processing*,[50,51] consists in the following three steps: (1) removal of the noble-metal fission products, (2) reduction of skull oxides to uranium metal and removal of essentially all the rare-earth, alkali, and alkaline-earth fission products, and (3) dissolution of the uranium in zinc–magnesium, which product solution is the feed to the subsequent retorting operation. In the latest series of plant-scale demonstration runs, more vigorous reaction conditions (higher temperature, longer contact times, and faster mixing) than in earlier runs[50,51] were employed.[45,47] Specifically, the noble-metal extraction step was carried out for 2 hr at 750°C; the reduction step was conducted for 2 hr, of which ¾ hr was required to heat the charge from 700°C to the operating temperature of 800°C; the mixing speed in both steps was 800 rpm. To verify the adverse effect of fluoride ion on fission-product decontamination in the noble-metal extraction step and the beneficial effect of fluoride ion on the reduction of uranium oxides in the reduction step, fluoride ion was added to the salt between the noble-metal extraction and reduction steps.[52] This procedure resulted in satisfactory removals[45] of molybdenum and ruthenium (varying from ~60% to ~90%) and excellent reduction[47] of uranium oxides (>99%) when 10 mole % fluoride ion was added as CaF_2 just prior to the reduction steps.

As in earlier runs, mechanical operations, namely, charging of materials, heating, mixing, sampling, and transferring molten metals and fluxes from the furnace to exterior receivers, were performed without difficulty.[45] The fume-control system,[53] which is connected to the furnace charging port and the transfer receiver, satisfactorily prevented the escape of metal and salt fumes to the inert-atmosphere enclosure in which the reduction furnace is installed.[45]

The final step in the skull-reclamation process consists in retorting, or solvent evaporation, to recover the product uranium from the zinc–12 wt.% magnesium–12 wt.% uranium ingot cast from the product solution that is transferred out of the reduction furnace. The retorting procedure consists in distillation of the magnesium–zinc under vacuum (~10 torrs) at 650 to 750°C from the uranium product solution, followed by melting of the uranium at approximately 1200°C to form a button. The same thixotropically cast beryllia crucible has now been used successfully in 10 plant-scale retorting runs.[46]

A clean uranium product can be obtained by retorting only if the residual flux is removed from the zinc–magnesium–uranium product solution before the solution is transferred to the beryllia retorting crucible. In small-scale experiments[46] and then in full-scale experiments,[47] salt flux was successfully removed from molten zinc–magnesium alloy when the material was poured through Fiberfrax strainers at temperatures ranging from 600 to 775°C. The Fiberfrax was preferentially wetted by the flux, and the clean metal, essentially free of flux, passed through the strainer. In the full-scale experiments, visual examination indicated no holdup of product metal on the strainer.[47]

Several uranium product buttons obtained in the retorting of zinc–magnesium–uranium product solutions have been analyzed by X-ray fluorescence techniques for fission-product elements. Results[46] confirm satisfactory overall molybdenum removals of 60 to 70% and ruthenium removals of 80%.

Operation of the retorting equipment in the current runs was very satisfactory. Improved control of retorting temperature and pressure eliminated the "bumping" that had occurred in earlier runs. Retention of zinc–magnesium alloy by the retorting apparatus was excellent with only negligible amounts escaping from the apparatus. At the conclusion of each run, the uranium product button was readily dumped from the beryllia crucible.[46]

PURIFICATION OF URANIUM FROM FISSION PRODUCTS BY CHLORINATION

Another approach to the purification of uranium from fission products is discussed by Avogadro

et al.[54] This procedure consists in the dissolution of irradiated UO_2 by means of chlorination in an alkali–chloride melt followed by reduction with hydrogen to UO_2. The alkali metals, such as cesium, as well as the alkaline earths, such as barium, and the rare earths, such as lanthanum, remain in the bath. Cerium and zirconium–niobium precipitate with the uranium. If only a small fraction of the UO_2 is precipitated, a logarithmic distribution of the two last-mentioned elements between the salt bath and the precipitated UO_2 is observed. This distribution allows a separation of these two elements from the bulk of uranium remaining in solution. With an artificial mixture of all elements with fission yields greater than 1% (simulating a burnup of 3%), the decontamination factors obtained by precipitation of 5% of the original charge of UO_2 were 1000 for zirconium–niobium and 7 for cerium. The elements tellurium, molybdenum, and ruthenium were separated by means of volatilization of the chlorine compounds.

Metal Purification and Preparation Processes

PURIFICATION OF PLUTONIUM BY ELECTROREFINING

Previous reviews[55–57] reported the successful demonstrations of continuous electrorefining of plutonium metal from plutonium trichloride at Hanford and Los Alamos. Soine[58] has continued this type of development and now reports on the preparation of high-purity plutonium by batch electrorefining. In electrorefining the passage of direct current results in the precipitation of plutonium metal at the cathode from migrating plutonium ions. The impurities which are more electropositive than plutonium tend to remain in the electrolyte, and those which are less electropositive tend to remain as a metallic anode. As long as plutonium is present, these conditions will exist. The electrolysis must be stopped when the transfer of impurities is still negligible.

Soine's electrolyte was composed of equimolar NaCl and KCl containing approximately 10 wt.% of plutonium as $PuCl_3$. The plutonium was introduced into the electrolyte by displacing magnesium (present as magnesium chloride). A two-piece noncemented cell, made from magnesia–magnesium titanate, provided resistance to thermal shock and enabled fairly short heat-up and cooling-off periods (~8 hr). Care was taken to ensure adequate stirring. The operating temperature was 800°C for most of the work. The cell was completely instrumented so that it required no attendance.

The process is capable of purifying 2.6 kg of plutonium metal per batch at a rate of 126 g/hr at a current of 50 amp. After purification the nonvolatile impurities were usually less than 100 ppm. Preliminary studies showed that americium, an impurity used as a starting material for making other transplutonium elements, concentrates in the electrolyte. Although some difficulties with the ceramic cell were experienced, it is felt these were solved and that the ceramic reliability should be 90% or greater.

FUSED-SALT ELECTROLYSIS

Two Japanese papers on the preparation of high-purity uranium metal by electrolysis have been presented by Kuroda,[59] and Nakajima and Kuroda.[60] In the first process[59] uranium is obtained by the fused-salt electrolysis of UCl_4. The source of the UCl_4 was U_3O_8 or UO_2 obtained by heating the precipitate from an aqueous solution of purified uranyl nitrate. The UCl_4 was then prepared by heating a mixture of the oxide and carbon in the presence of flowing chlorine in an electric furnace. The products of the reaction when UO_2 is the starting material are UCl_4, CO, and CO_2. Large crystals of UCl_4, which must be free of impurities, are desirable for the electrolysis. The vapor pressure of UCl_4 was depressed by carrying out the electrolysis in the presence of salts of alkali or alkaline-earth metals.

The second process[60] produces uranium with a 99.99% purity by fused-salt electrolysis in 20 wt.% UF_4–44 wt.% KCl–36 wt.% LiCl, followed by purification of the resulting crystal uranium by electron-impact techniques. The electrolytic cell, made of translucent quartz, was kept in an argon atmosphere, and electrolysis was carried out at 400 to 500°C. The voltage applied was 1.0 to 1.5 volts. The uranium obtained was washed by an ultrasonic wave of 28 kc/sec. The washed uranium crystal was melted and purified, either in an arc furnace or an electron-impact fusion furnace. Electrolysis was carried out with W–W or U–U electrodes. In general, the size of the crystals increased with decreasing applied voltage and the amount of impurities decreased but the amount of salt, KCl, LiCl, and others, increased. Small uranium crystals were desirable for the removal of contaminating salts by ultrasonic waves. Purification by an arc furnace was better than by conventional methods, but the removal of volatile impurities was not sufficient. Electron-impact fusion resulted in good removal of these impurities and aluminum, and there was no contamination from electrodes. The uranium crystal, after washing, had to be free of moisture; alcohol was used to dry the crystals.

A patent was issued to Benedict[61] on a method for the separation of plutonium values from uranium values by an improved electrolytic process. An improvement in the plutonium separation factor from 13 to 160 and an increase in the bulk density were brought about by using a fused-salt melt of equimolar lithium chloride and potassium chloride at a temperature of 600 to 625°C at a controlled cathode current density and by sparging the final electrolysis with a gas mixture of oxygen and chlorine.

Miscellaneous

Cairns,[62] in an Australian paper, reviewed available spent-fuel processes primarily with regard to

power fuels. Although emphasis is placed on aqueous processing methods, both pyrochemical and halide-volatility processes are considered. The author expects strong competition by the newer halide processes for treating power-reactor fuels.

Attention is called to two additional papers that have been previously reviewed and have now been republished. The first is on the fused-salt electrorefining of plutonium and its alloys, by Mullins and Leary,[63] originally reviewed as Ref. 36 in the nonaqueous processing subsection of the Spring 1965 issue of *Reactor Fuel Processing* and the survey article by Faugeras[64] on dry chemical processing of irradiated fuels. This latter article was originally reviewed as Ref. 70 in the nonaqueous processing subsection of the Spring 1966 issue of *Reactor Fuel Processing*.

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Section

IV

Reactor Fuel Processing

Waste Disposal

By P. Fineman

Treatment of Intermediate-Level-Activity Wastes

Ion Exchange and Electrodialysis

Mercer[1] at Pacific Northwest Laboratory (PNL) has studied the cation-exchange removal of trace quantities of radioactive cesium and strontium from solutions containing single or multiple competing nonradioactive cations. With the data obtained in this study, it is possible to predict theoretically the behavior of ion exchangers in the treatment of waste solutions. In the report of this study, Mercer has presented trace cesium and strontium selectivity coefficients* for 4 organic and 12 inorganic cation exchangers. The selectivity data were obtained for the following individual cations: H^+, NH_4^+, Na^+, K^+, or Ca^{2+}. For trace cesium the inorganic exchangers† generally exhibited greater cesium selectivity than the organic exchangers‡ and showed higher cesium selectivity in the presence of NH_4^+ or K^+. For trace strontium the organic exchangers, in general, manifested greater strontium selectivity and displayed a higher strontium selectivity in the presence of H^+, NH_4^+, Na^+, or K^+ than in the presence of Ca^{2+}. Some exceptions were noted, however. Four of the synthetic and natural zeolites showed quite high strontium selectivity in the presence of Na^+ and Ca^{2+}.

By means of mass-action equations, which involve the selectivity coefficient of the trace ion and the concentrations of competing ions, Mercer has also shown that good estimates can be obtained of the distribution coefficients for cesium and strontium in systems containing two competing cations. Good agreement was found between computed and experimentally determined distribution coefficients for various systems. Computed distribution coefficients were also used to calculate cesium-ion breakthrough curves. These curves were compared with actual curves determined previously for two pilot-plant runs in which cesium was removed from a Purex tank-farm condensate waste containing ammonium and sodium ions as the major competing ions. The slopes of the computed breakthrough curves agreed well with the actual curves for the range covered. For a cesium breakthrough point of 1%, the computed points were within 20% of the experimental ones.

*The selectivity coefficient, which is calculated from experimental data, is a measure of the preference of the exchanger for one ion relative to the other. A general equation for computing the selectivity coefficient is presented by Mercer in his report.

†The following types of inorganic cation exchangers were used in this study: compounds of zirconium (phosphate, molybdate, or tungstate form), ammonium molybdophosphate, processed glauconite, aluminosilicate gel, synthetic zeolites (erionite, chabazite, faujasite, morganite), and natural zeolite (clinoptilolite). Their exchange capacity ranged between approximately 0.2 and 4 meq of Na^+ per gram of exchanger.

‡All the organic cation exchangers tested were of the high exchange capacity type (~4 meq of Na^+ per gram of exchanger) sulfonated polystyrene resins.

RUTHENIUM REMOVAL BY ELECTRODIALYSIS AND ELECTRODEIONIZATION

Workers at PNL are evaluating electrodialysis and electrodeionization techniques as possible methods for the removal of ruthenium from intermediate-level-activity wastes (ILW).[2-4] Electrodialysis refers to ion transport through permeable membranes under the influence of an applied electric field. The electrodialysis process is economically competitive with ion-exchange or evaporation processes for the treatment of radioactive solutions containing about 500 to 10,000 ppm dissolved solids and, in particular, for those wastes containing dissolved solids between 1000 and 3000 ppm. At low electrolyte concentrations (less than about 500 ppm), the operating efficiency of electrodialysis decreases rapidly owing to high solution resistances and membrane polarization. Strongly ionized resins, when placed in the electrodialysis compartments, can overcome this increased resistance by serving as an ion-conduction medium. This technique is referred to as electrodeionization. In electrodeionization sufficient polarization occurs to dissociate water electrolytically in order to effect regeneration of the membranes and resin. The feed materials used in the investigation were acid (1 to $3 \times 10^{-2} M$ HNO_3; 10^{-2} μc Ru/ml) and alkaline (2 to $12 \times 10^{-3} M$ NH_3; 10^{-3} μc Ru/ml) intermediate-level-activity condensates.

Electrodialysis Treatment of Acid-Condensate Wastes. Three-, seven-, and twenty-cell units were tested using acid condensate to evaluate ruthenium and nitrate removal by electrodialysis.[3,4] Ruthenium-ion removal relative to nitrate-ion removal was ob-

served to be slow, only approximately 60% of the original ruthenium ion being removed during the time required to remove 90% of the original nitrate ion. In other tests to improve ruthenium removal, the denitrated acid waste from the electrodialysis unit was passed through a mixed-bed ion exchanger. For this method of treatment, the overall ruthenium decontamination factor was 11. This process, electrodialysis plus mixed-bed ion exchange, has limited utility for treatment of ILW since ruthenium decontamination factors of 20 to greater than 100 are often required.

Electrodeionization Treatment of Acid- and Alkaline-Condensate Wastes. In electrodeionization work[3,4] three-cell units were tested for the removal of ruthenium from acid- and alkaline-condensate wastes. The deionization compartment contained a mixture of three volumes of Dowex 1 and two volumes of Dowex 50W. The results of tests with both types of condensate showed that 95% ruthenium removal and a fiftyfold volume reduction can be readily achieved. Further evaluation of the electrodeionization process is planned.

Incorporation in Asphalt

At Oak Ridge National Laboratory (ORNL), work is continuing on the fixation in emulsified asphalt* of the concentrate produced from the ORNL waste-evaporator processing of aqueous ILW.[5,6] The fixation process consists in incorporating the waste concentrate into the asphalt by mixing, heating the mixture to 130 to 160°C, holding at this temperature until the water has evaporated, and then pouring the mixture into a container. In recently reported laboratory work,[6] hot-cell fixation tests were successfully carried out using actual concentrated ORNL ILW plus added aged mixed fission products to a final radioactivity level of about 5 curies/gal. (For one of the tests, the radioactivity in the feed was increased to 8.8 curies/gal.)

The condensates collected from the fixation of the concentrated ILW in asphalt contained essentially only entrained ^{137}Cs; insignificant amounts of ruthenium were found in the condensate. Deentrainment devices on the asphalt fixation vessel should minimize fission-product contamination of the condensates; none were used in these experiments. The solids content of the asphalt products from these tests amounted to about 60 wt.%.

Static leaching tests were conducted in demineralized water with the asphalt products produced from the feeds containing about 5 curies of radioactivity per gallon. At the end of five months, the sodium and ^{137}Cs leach rates approached a steady-state rate of about 2×10^{-4} g/(cm^2)(day). This leach rate is considered satisfactory for permanent disposal by burial in steel drums.

The asphalt product from the feed containing 8.8 curies of radioactivity per gallon was placed in a sealed container connected to a pressure-recording device to determine the amount of gas evolved (radiolytic decomposition) from self-irradiation. No measurable amount of radiolytic gas was generated during the five-month test period. Over this time interval the asphalt product received an estimated internal dose of about 1.2×10^7 rads.

*The asphalt used in these studies is defined in Federal Specifications SS-A-6746 (Emulsion Paving Asphalt) as type RS-2, a rapid-settling high-viscosity emulsified asphalt for surface treatment. The material used contained 35 wt.% H_2O.

Conversion of High-Level-Activity Wastes to Solids

Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes

A symposium[7] was held at Richland, Wash., Feb. 15 to 18, 1966, under the sponsorship of the U. S. Atomic Energy Commission. The symposium covered the developments in high-level-activity waste management and technology that have taken place since 1962, when a similar meeting on this subject was held in Vienna.[8] Some 40 papers were presented in nine sessions which covered the following topics:

1. Future high-activity waste-management requirements and problems
2. Processes for high-activity-waste solidifications
   a. Bench-scale and pilot-plant process-development studies
   b. Active process demonstration status
3. Characteristics of final products
4. Final storage or disposal concepts
5. High-activity waste-management economics

All the papers presented at the symposium will be published in the proceedings of the symposium. Some of the papers[9] are summarized below.

WASTE MANAGEMENT

Blanco and associates[9] at ORNL pointed out that high-level-activity aqueous wastes produced in all countries are stored in tanks and that this practice will continue for an interim period until development of a safer or more economical disposal method is completed. They suggest that the solidification of these wastes (as a calcine or a glassy solid) and their permanent storage in a dry underground environment offer a safer ultimate solution of the problem since this approach reduces the mobility of the vast quantities of long-lived fission products produced in power reactors.

Economic evaluation of the two alternative treatment methods (tank storage or solidification and storage) showed that the costs were comparable and

amounted to about 1% of the cost of nuclear power. They believe, however, that it is advantageous to choose the safest method, that of conversion to a solid form and storage.

Blanco and associates also stated that the amount of radioactive waste produced at a fuel-processing plant was not expected to be a limitation on the capacity of the plant. In an expanding nuclear economy, the quantity of ^{85}Kr and tritium (Ref. 10) released can impose severe operational problems unless these gases are retained.

Information on the quantities of high-level-activity wastes which would arise from the processing of spent fuel was also presented by Blanco and associates. In the United States the annual production rate for wastes will increase from 31,000 gal/year in 1970* to 3.4 million gal/year in 2000. If this waste were stored as a liquid over this period, about 31 million gallons would be accumulated by 2000. However, if this waste were stored as a solid, the rate of waste solidification would increase from 310 cu ft/year in 1970 to 34,000 cu ft/year in 2000. The accumulated volume in storage rises from 550 cu ft in 1970 to 310,000 cu ft in 2000.

FLUID-BED CALCINATION

Lockard and Garner[9] at the Idaho Chemical Processing Plant (ICPP) have examined the economics of storing the liquid wastes generated at the ICPP as either an acidic or neutralized liquid or as a calcined solid. The liquid wastes are those produced from the processing of zirconium-alloyed or aluminum-alloyed fuel. Their data indicated distinct advantages in terms of economics and safety for storage of wastes as calcined solids. To determine the optimum approach for this type of storage, the authors investigated the economic effects of interim liquid storage, interim solids storage, and different solids storage temperatures.

Rhodes[9] described the design of new bins[11] for the storage of calcined solids from the Waste Calcining Facility (WCF) at the ICPP. The construction of seven new storage bins of type 304 stainless steel and the cylindrical concrete vault in which the bins will be placed has been completed.[12] The bins were designed to contain calcine having a centerline temperature of 700°C as contrasted with the centerline limit of 400°C for the present storage units. Experimental data indicated that the storage of calcine at 700°C will not create problems because of migration of fission products.[13] The seven bins have a combined storage capacity of approximately 30,000 cu ft and will meet the currently estimated storage requirements[9] for the ICPP until about 1972. The fission-product decay heat from the stored solids within the bins will be removed by natural convection of air flowing past the bins. If a bin failure should occur so that radioactive solids are released into the vault, the flow of cooling air will be shut off automatically. Cooling will then be accomplished by radiation and conduction of heat through the vault wall and into the surrounding soil. This method of heat removal has been tested on the present storage bins by shutting off the cooling air and has been found to be completely satisfactory and reliable. The temperatures of the solids and bin walls increased only by about 50°C. The design of the storage bin will allow the stored solids to be retrieved in the future for the recovery of valuable by-products or for conversion to a glass form[14] for even safer storage.

The successful calcination of acidic aluminum nitrate waste in the WCF has led to the consideration of calcining other wastes now in storage or scheduled to be produced at the ICPP.[15] Wastes being considered include aluminum nitrate wastes containing high concentrations of zirconium fluoride, sodium ion, or ammonium ion and stainless-steel nitrate–sulfate wastes. Preliminary pilot-plant tests have been conducted using simulated aluminum wastes. The results of the pilot-plant tests and the proposed method of handling the stainless-steel wastes were reported by Bailey and coworkers at the ICPP.[9] The results of the tests indicated that all the new types of aluminum nitrate wastes can be calcined satisfactorily in the WCF provided that (1) the wastes high in zirconium fluoride have calcium added to complex the fluoride, (2) the wastes high in sodium ion have sugar added during calcination to decompose the nitrate, and (3) the wastes high in ammonium ion are either handled alone or blended with the regular acidic aluminum nitrate wastes. The stainless-steel nitrate–sulfate wastes pose potential corrosion problems during calcination because of the possible volatilization of the contained sulfate. Laboratory tests have shown that the volatilization of sulfate can be reduced to less than 1% by the addition of aluminum nitrate. It is planned therefore to blend the stainless-steel wastes with the regular acidic aluminum nitrate wastes before calcining.

CONVERSION TO GLASSES

Oak Ridge National Laboratory has under development processes for converting high-level-activity wastes to stable glassy solids of low solubility.[16] The evaluation of these processes requires a knowledge of the properties of the solids formed, such as melting or softening point, density, fraction of the product that is from the waste, solubility in water, thermal conductivity, viscosity, and density of the molten material. Godbee and associates[9] have summarized the glassy-solids development studies conducted at ORNL in which more than 500 different melts* were

*The installed nuclear power in the United States is expected to range from 7000 Mw(e) in 1970 to 734,000 Mw(e) in 2000.

*The composition (and most of the other properties) of all the melts studied and the FORTRAN II code for storing and retrieving this information are given in a report by ORNL workers.[17]

prepared. Simulated wastes of the following types were used in the melt studies: (1) Purex, a nitric acid waste from aluminum-clad uranium fuels; (2) Darex, a stainless-steel nitrate waste from stainless-steel-constituted fuels; and (3) TBP-25, an aluminum nitrate–nitric acid waste from enriched-uranium–aluminum alloy fuels. Most of the glassy solids were prepared with phosphates as the main matrix material. A few silicate and borate melts were also studied. In addition to phosphate, silicate, or borate, the other main glass-forming additives were lithium, sodium, aluminum, calcium, and lead.

The melting or softening points of the glassy solids ranged from 600 to 1050°C. Densities of the solids were about 2 to 5 g/cm^3. The weight fraction of the product that represents solids from waste varied from about 0.15 to 0.70. Solubilities, as indicated by leach rates, changed markedly with composition. For the best products these leach rates are of the same magnitude as those of commercial glasses, i.e., 10^{-4} to 10^{-7} g/(cm^2)(day). Thermal conductivities ranged from about 1 to 1.7 Btu/(hr)(ft)(°F) over the temperature of interest—about 200 to 1600°F. Viscosities of the melts varied from about 5 to 225 poises at 900°C. (The viscosities of the phosphate melts measured are about 100 to 1000 times lower than those of commercial glasses.)

These properties show that glassy solids which are relatively low-melting, insoluble, pore-free, and dense can be formed containing a large fraction of solids from the waste. The better products represent volume reductions comparable to those obtained with calcined waste (no glass-forming additives added). Their thermal conductivities are 2 to 10 times higher than those of calcines or powders representing similar volume reductions.

Under the self-heating conditions that would exist in high-level-activity waste storage, devitrification of glassy melts can occur and result in increased solubility of a glassy melt. Upson[9] at PNL stated that, even though it may be possible to select melt compositions in which devitrification involves negligible mechanical damage, a more stable waste-storage form may be that of a polycrystalline ceramic. He believes that, since the theory and techniques of nucleated crystallization are becoming sufficiently known for practical application,[18,19] it may be possible to produce, as a possible waste-storage form, a microcrystalline material similar to Pyroceram (a product of Corning Glass Works).

Fission-Product Recovery

As part of the Hanford program for the management of wastes and recovery of fission products, plant-scale facilities to recover megacurie quantities of selected fission products from Redox- and Purex-plant wastes are planned.[20] Laboratory, pilot-plant, and plant-scale investigations in support of the development of the process flow sheets to be used in these facilities are in progress. A facility for the packaging of up to 1-megacurie quantities of fission products (sorbed on an aluminosilicate bed) in all-welded stainless-steel containers is being designed.[21] (Jansen and DeMier[22,23] at PNL have presented dimensionless correlations useful in describing the transient thermal conditions of various types of containers in which heat-generating radioactive materials are stored. The maximum temperatures attained are presented as functions of various parameters.)

Promethium

In a successful plant-scale demonstration of a promethium recovery and purification flow sheet, the suspended slurry containing about 0.003 wt.% ^{147}Pm from one of the stored alkaline plant wastes was processed for the recovery of promethium.[24] The flow sheet tested consisted of the following steps:

1. Centrifuging the slurry and then leaching the solids with nitric acid to solubilize the promethium and other associated rare earths.
2. Selectively precipitating the promethium and rare earths (principally cerium) as oxalates to separate them from iron, ruthenium, zirconium–niobium, and strontium.
3. Dissolving the promethium–rare-earth precipitate in nitric acid and then separating the promethium from the cerium and other nonradioactive contaminants (principally iron, lead, and strontium) by solvent-extraction processes utilizing di-2-ethylhexyl phosphoric acid (D2EHPA).
4. Simultaneously decomposing the excess nitric acid in the promethium nitrate product solution with sugar and concentrating the product solution.
5. Chromatographically separating the promethium from the remaining rare earths (principally, neodymium, samarium, europium, lanthanum, and praseodymium) by passing the concentrated product solution through an ion-exchange column containing Dowex 50W (8% cross-linked).

With this flow sheet, approximately 45,000 curies of promethium at 98 wt.% purity was obtained.

Cerium

A recently developed process[25-27] for separating cerium from other rare earths consists of the following steps:

1. Coextraction of the rare earths from an aqueous fission-product solution [complexed with *N*-hydroxyethylethylenediamenetriacetic acid (HEDTA) or other suitable complexing agent to prevent extraction of unwanted ions such as lead] into D2EHPA containing a hydrocarbon diluent.
2. Partition of the cerium from the other rare earths by stripping the latter into 2*M* HNO_3 contain-

ing persulfate and silver ions.* The cerium is oxidized to Ce(IV) and remains in the D2EHPA phase.

3. Stripping the cerium from the solvent with 2*M* HNO_3 containing 0.05*M* $NaNO_2$ to reduce the Ce(IV) to Ce(III).

As originally developed, the process used batch contacts to transfer the rare earths to and from the solvent phase.[26] Several problems were initially encountered in the plant-scale application of the process in recovering cerium and trivalent rare earths from a Purex-plant waste. These problems and their solutions, which are described in detail in a report by Bray and Roberts[27] at PNL, are briefly summarized here. Manganese, which is present in one of the Purex wastes because of its use in solvent cleanup, interfered seriously in the persulfate oxidation of cerium. Separation of the manganese and the cerium–rare earths was accomplished by precipitating the cerium–rare earths with $NaHSO_4$, decanting and metathesizing the precipitate with sodium hydroxide, dissolving the resulting precipitate in nitric acid–HEDTA, and finally coextracting the cerium–rare earths into D2EHPA. Repeated use of the D2EHPA solvent in the partition step became marginal because radiolysis of the solvent generated reducing impurities that consumed the persulfate and prevented oxidation of the cerium to the quadrivalent state. The radiolysis effect was markedly reduced, and high cerium distribution ratios were maintained by substituting a straight-chain hydrocarbon diluent for the branched-chain diluent (Soltrol-170) previously used. During the second D2EHPA extraction cycle for the purification of cerium-free rare earths, loss of trivalent rare earths, as rare-earth double sulfates, was encountered when the *p*H was adjusted (>*p*H 1.5) for this extraction cycle. The addition of HEDTA to these solutions prevented precipitation of the double sulfates at *p*H values greater than about 2.8.

It was recognized, however, that a continuous countercurrent solvent-extraction system (pulsed columns) could offer a substantial improvement in efficiency and control.[26] Therefore pilot-plant studies with pulsed columns were carried out using simulated feed solutions containing added rare-earth tracers. The effect of stream compositions, flow rates, and temperature on cerium–rare-earth separations were investigated. Studies were also made of the extraction kinetics of rare earths from an HEDTA-complexed feed ($^{152-154}Eu$ was used as tracer to represent a slow-acting rare earth).

The proposed continuous separation process was successfully demonstrated. Satisfactory separation of the cerium and other rare earths was achieved using 2*M* HNO_3 strip solutions containing 0.3*M* persulfate and 0.0012*M* to 0.012*M* silver ions. Typical cerium contamination in the rare-earth product stream was less than 0.3% of that entering the column with aqueous extractant flow rates ranging from 10 to 20% of the organic-solvent feed flow. Corresponding rare-earth losses in the effluent organic solvent stream were 3% or less with a 10-ft-long stripping section. A short scrub section, about 2 to 4 ft long, was required to remove residual Ce(IV) from the aqueous product. The scrub flow of fresh solvent was 20% of the organic-solvent feed flow. Operating at elevated temperatures (30 to 50°C) and using a top interface to increase the aqueous-phase residence time (typically 80 to 180 min) contributed to high cerium separation and low rare-earth losses.

More than 99% of eurpoium was extracted when the column was operated at 50°C and the aqueous phase was continuous to maximize the aqueous-phase residence time.

This continuous process was also satisfactorily demonstrated in a plant-level-activity run using a feed prepared from a Purex waste.

*The cerium-free rare earths are subsequently purified from sulfate and silver ions by a second D2EHPA extraction cycle.

Other Literature

Girdler,[28] Savannah River, discusses the probable cause for the leaks that developed in 4 of the 16 underground storage tanks used for storage of alkaline radioactive waste from the separations area at Savannah River. The carbon-steel tanks are 75 to 85 ft in diameter and were field-erected by welding; the welds were not stress relieved. The investigation of these cracks revealed no correlation with the history of the construction or usage of the tanks. Stress-corrosion cracking arising from the chemical action of waste on steel is the most likely explanation of the leaks. Similar stress-corrosion cracks in tanks of this type can be prevented by full stress relieving after welding has been completed.

The waste-management practices at Savannah River,[29] Argonne National Laboratory and Los Alamos Laboratory,[30] and Lawrence Radiation Laboratory (Livermore)[31] are discussed in several reports. Girdler[29] reviewed the handling of low-level-activity and medium-level-activity liquid wastes at Savannah River. Various decontamination processes are employed to handle these wastes. A waste stream may be subjected successively to one or more of the following decontamination processes: (1) storage for settling and radioactive decay, (2) distillation, (3) ion exchange, and (4) seepage through natural soil. The costs for each method are given. Emelity and Christenson, Los Alamos, and Kline, Argonne,[30] pointed out that the waste-management philosophy at both laboratories is the same, namely, the concentration and containment of the activity. Operational procedures for final containment differ at the two sites in that all wastes generated at Los Alamos are buried on site, whereas no wastes are permanently stored at Argonne. Kvam[31] at Lawrence Radiation Laboratory states that the waste-management

program has two main functions: (1) to develop methods of reducing waste volume and (2) to dispose of radioactive wastes. He discusses several methods of disposing of mixed alpha- and beta-contaminated wastes by solidification with Portland cement and solar evaporation. He describes various methods of packaging solid waste in drums, concrete containers, and polyurethane foam and the use of hydraulic compression to pack the containers.

The International Atomic Energy Agency, Austria, has issued a new publication in its Safety Series, Radioactive Waste Disposal into the Ground.[32] The information on disposal into the ground has come from establishments that routinely practice ground disposal on a large scale. Included in this work is information on site characteristics affecting ground disposal, chemical reactions of wastes in the ground and their physical behavior, modes of release, evaluation of sites and methods of ground disposal, standards and control techniques, pretreatment (conversion into solidified forms) for ground disposal, physics and chemistry of the movement of radioactive wastes in the ground, ground-disposal operations, and methods of site investigation.

Upson[33] at PNL has summarized the pilot-plant-scale tests demonstrating the technical feasibility of the Brookhaven continuous phosphate-glass process.[34] This process consists of adding glass-forming chemicals (principally phosphoric acid) to the aqueous waste and converting the mixture directly to a glass, with no intermediate drying or calcination step. In these tests phosphate glass was produced from actual plant-level-activity Purex 1WW waste.[33]

A study is under way at PNL on the hazards of shipping high-level-activity wastes fixed in a phosphate-based matrix.[35] Because a shipping accident involving such a ceramic-fixed waste might occur and result in a high-temperature fire, the possibility of airborne fission-product release from these wastes at high temperatures is being investigated. The results of this study are summarized by Albrethsen, PNL.[36] Tests were conducted with nonradioactive samples of phosphate-based ceramics containing added fission products (cesium, strontium, cerium, or ruthenium). The compositions of the ceramics corresponded to wastes produced in the reprocessing of power-reactor fuel elements irradiated to 100,000 Mwd/metric ton. A high release rate ($\frac{1}{2}$%/hr at 1100°C) was observed for cesium, whereas fractional release rates (10^{-3}%/hr) were noted for cerium, ruthenium, and strontium at the same exposure conditions. Volatilization of the cesium was established as the predominant mechanism of fission-product release. Varying the phosphate and the fission-product contents did not appreciably affect the release rate.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

By J. J. Barghusen and P. A. Nelson

Production and Properties of Uranium Dioxide

Processes for Producing UO_2

Gas–solid reactions, particularly the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rates of these reactions are determined by the structures of the solid surfaces which, in turn, are modified as the reactions progress. The reactivity of uranium dioxide toward hydrogen fluoride is highly dependent on the nature of the UO_2 surface. A highly unreactive form of UO_2 is produced by reduction of UO_3 derived from thermal denitration of uranyl nitrate solutions in a fluid-bed reactor. A patent was issued[1] on a method for producing a reactive grade of UO_2 from fluid-bed UO_3. The method involves hydrating the UO_3 by mixing the powder with a slight excess of water at 80°C to form a paste of $UO_3 \cdot 2H_2O$. When UO_3 particles and water are mixed at high speed, the solid particles fracture and the result is a rapid rate of hydration. About 20 min is required to complete the hydration. The hydrate paste is dried for 1 hr at 80°C, and a granular form of $UO_3 \cdot 2H_2O$ is thus produced. This material is then reduced to UO_2 by reaction with hydrogen at 500°C. Laboratory-scale tests for preparation of UF_4 have shown that UO_2 derived from hydrated UO_3 is highly reactive toward hydrogen fluoride. The time required in both the reduction and hydrofluorination steps is markedly less with the hydrated material in comparison to that required in processing UO_3 derived from thermal denitration.

A method for producing microspheres of uranium dioxide based on sol-gel technology is being developed at Oak Ridge National Laboratory (ORNL).[2] The sol preparation step involved the reduction of U(VI) in solution by hydrogen with the use of a palladium-impregnated thoria catalyst followed by precipitation of U(IV) hydrous oxide with a solution containing 3.0*M* NH_4OH–0.5*M* $N_2H_4 \cdot H_2O$. Precipitation phenomena and characteristics of the precipitate were improved by making the U(IV) solution 0.3*M* in formic acid prior to precipitation of the hydrous oxide. After precipitation of U(IV) was completed, the solution was filtered and the filter cake washed. The hydrous oxide cake was then heated to 60°C and vigorously stirred until the oxide was transformed into a fluid sol. Gel microspheres were formed by dispersing the sol as drops in a column of drying solvent (2-ethyl-1-hexanol) and fluidizing the drops during drying and gelation. This technique for producing gel spheres has been successively demonstrated with thoria systems.[3] The gelled spheres were then fired to form strong, dense UO_2 particles.

The carbon content of the dried gel spheres was 2 to 7 wt.%. Fired UO_2 spheres frequently contained up to 4000 ppm carbon.[2] The presence of the carbon has been attributed to incomplete removal of the drying solvent during the firing step. Several techniques for removing the solvent were evaluated, and a procedure based on steam stripping using mixtures of steam and either hydrogen or carbon monoxide was most effective.

Several firing procedures were evaluated in an effort to reduce the carbon content of the microspheres. Heating the spheres in air to 1150°C was successful in removing carbon from the final product, but the fired spheres had low crush strength and low density. Particles fired for 4 hr in hydrogen at 1150°C exhibited high crush strengths but contained 2000 to 5000 ppm carbon. Particles that were heated under an atmosphere of CO_2 at temperatures up to 900°C and then fired in hydrogen at 1150°C contained less carbon but exhibited lower crush strengths. Development work is continuing in an effort to establish drying and firing conditions that will lead to the production of strong spheres with low carbon content.[2]

The encapsulation of uranium dioxide particles within a metallic coating provides a potentially significant reactor fuel material resistant to corrosion and radiation damage for use at conditions of high temperature and high burnup. Sari and Pivato[4] have evaluated several techniques for applying metallic coatings to UO_2 particles with diameters between 100 and 200 μ. Compact nickel coatings were obtained by the chemical reduction of Ni^{2+} ions in an aqueous solution of an alkaline hypophosphite. Uniform, ad-

herent deposits were achieved by conducting the reduction at temperatures between 85 and 90°C. Agglomeration of the UO_2 particles is avoided if the particles are kept in motion throughout the coating process.

Oxidation Behavior of Uranium Dioxide

Bulk oxidation of UO_2 at temperatures above 60°C occurs at the same rate in air as in oxygen. Imris[5] has investigated the oxidation of UO_2 and has observed that the oxidative properties of UO_2 should not be linked with the conditions of preparation of UO_2 but directly with the particle size of the UO_2.

The oxidation behavior of four different varieties of uranium oxide samples was studied by Amanuma and Sakamoto.[6] The uranium oxide samples were finely powdered UO_2, massive fused UO_2, electrodeposited UO_2, and single crystals of cubic U_4O_{9-x}. When each sample was heated in air, the following transformations were observed: UO_2 or U_4O_{9-x} phase (cubic) → U_3O_7 phase (tetragonal) → U_3O_8 phase (hexagonal). The transformation from the cubic to the tetragonal phase occurred in the temperature range 200 to 400°C, and the tetragonal to hexagonal phase transformation occurred in the temperature range 340 to 425°C. In some cases the transformation from the cubic phase to the tetragonal phase was not clearly observed, and the sample appeared to be transformed directly to U_3O_8. In spite of the remarkable difference in external appearance, electrodeposited UO_2 and U_4O_{9-x} showed nearly identical oxidation behavior.

Through the use of high-temperature X-ray diffraction analyses and electrical-conductivity measurements, Bessonov et al.[7] have followed the phase transformation in the oxidation of UO_2 in the temperature range 200 to 337°C. The results of this study have confirmed that the phase transformations are $UO_2 - UO_{2+x(\max.)} \rightarrow \beta\ UO_2(U_4O_{9\pm y}) \rightarrow \gamma\ UO_2$ (tetragonal phase $UO_{2.33}$) → $\alpha\ U_3O_8$ → $\beta\ U_3O_8$. It was possible to discern clearly the conversion of alpha U_3O_8 to beta U_3O_8 at temperatures near 340°C.

The behavior of UO_2 in high-temperature environments is of fundamental interest in the prediction of the performance of UO_2 as a reactor fuel. Chapman and Meadows[8] have studied the volatility of $UO_{2\pm x}$ and the phase relations in the uranium–oxygen system at temperatures between 1100 and 2200°C. The results of the study suggest that UO_4 (gas) is the uranium-bearing vapor species above $UO_{2\pm x}$. Evidence supporting the existence of UO_4 (gas) included the volatilization of material with an oxygen-to-uranium ratio of 4 during the decomposition of $UO_{2.2}$ to nearly stoichiometric UO_2 in vacuum above 1500°C and the observed dependence of the rate of vaporization from UO_{2+x} on oxygen pressure at temperatures between 1200 and 1500°C.

Sintering Properties of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered uranium dioxide as the fuel. This fuel must be of high density (>93% of theoretical density) to assure dimensional stability of the fuel and a high degree of fission-gas retention. The development of economic processes for the production of sintered UO_2 of high density is of fundamental importance in reactor fuel concepts. Nishijima, Kawada, and H. Kitagawa[9] have described a process for fabricating UO_2 pellets. A system of rotating rollers was employed for the comminution of the UO_2. The product of the comminution step was said to possess a particle-size distribution highly suitable for sintering to high-density bodies. Stable UO_2 granules were prepared from powder by blending the powder with an organic binder containing 1 to 5 wt.% paraffin, 0 to 3 wt.% stearic acid and 1 to 5 wt.% polyethylene glycol in CCl_4. The CCl_4 was removed by drying the mixture after granulation. The granules were metered by volume to an automatic press for fabrication of pellets. The authors discuss in detail the methods used to achieve the precise dimensional and density specifications required in pellet fabrication.

Uranium dioxide powders are produced by several different methods, and the sintering properties of the powders are greatly affected by the preparation method. Moorthy[10] has examined in detail the influence of the UO_2 preparation method on the microstructure of sintered UO_2 pellets. Uranium dioxide powders were prepared by three methods: calcination and reduction of ammonium diuranate (ADU) precipitated by ammonium hydroxide or precipitated by urea, and calcination and reduction of uranyl tannate. The crystallite size of UO_2 powder derived from uranyl tannate was smaller than the crystallite size of powder derived from ADU. The density of powders from tannate was significantly higher than that of the other two powders.

Samples of each of the three powders were pressed at 30 tsi into pellets that were then sintered in a hydrogen atmosphere at temperatures of 1300, 1400, 1500, and 1600°C. Two heating rates were compared: 8°C/min to the specified sintering temperature and 8°C/min to 800°C followed by 2°C/min to the required sintering temperature. In all samples greater densification of pellets resulted when the pellets were heated to the sintering temperature at the lower rate. The maximum densification occurred at an optimum firing temperature, specific for each variety of UO_2 powders. Samples of UO_2 derived from tannate attained a maximum sintered density at 1400°C, whereas UO_2 from ADU precipitated by NH_4OH showed a similar maximum density at 1500°C. No such maximum was observed at temperatures up to 1650°C for UO_2 samples derived from ADU precipitated by urea.

The high initial densification in samples from uranyl tannate may be attributed to the small crystal-

lite size and high powder density of the UO_2 powder. Once high density was attained in the pellet and open porosity eliminated, further densification proceeded slowly. For pellets derived from ADU, a higher sintering temperature was required to attain high pellet density. The decrease in density at temperatures greater than the optimum sintering temperature as observed with UO_2 from uranyl tannate may be explained by plastic flow. If the rate of plastic flow is sufficient to allow interparticulate voids to be filled in without sealing the voids, densification occurs by elimination of open porosity. This evidently occurs at temperatures below 1400°C. However, if the rate of plastic flow is too rapid, voids become entrapped within the oxide matrix. At higher sintering temperatures, above 1400°C, the gases in the closed pores expand and cause an increase in the size of the pores and an overall increase in the volume of the pellet, thus resulting in a lower sintered density.

The presence of TiO_2, even in very small quantities (0.01 wt.%), promotes the densification of UO_2 and lowers the optimum sintering temperature for obtaining maximum densification in a hydrogen atmosphere.[11] Grain development and grain growth in UO_2 are promoted by the presence of titania.

Ram, Gadiyar, and Jena[12] have studied the kinetics of sintering of UO_2 compacts prepared from ADU in hydrogen in the temperature range 950 to 1500°C. From the results of this study, an activation energy of 102 ± 10 kcal/mole was calculated for the sintering process. The authors pointed out that this value agrees well with a value of 108 kcal/mole which has been calculated from experimental data for uranium-ion diffusion over the temperature range 1300 to 1550°C.

Production of Plutonium Compounds

Reduction of Plutonium by U(IV)

The standard feed for the production of plutonium metal or compounds is a dilute solution of plutonium in nitric acid from the Purex solvent-extraction process. In the Purex process, plutonium is partitioned from uranium by the use of a selective reducing agent for converting Pu(VI) to Pu(IV). Currently, ferrous sulfamate–sulfamic acid is employed as the reductant. Considerable interest has been shown in the use of U(IV)–hydrazine solutions as reducing agents in the solvent-extraction separation and recovery of plutonium from uranium. Since U(IV) adds no extraneous ion to the process, both the corrosion rate of process equipment and the amount of radioactive waste to be stored would be decreased in comparison to the Fe(II) process.

Mendel,[13] in a series of laboratory tests, has investigated the use of U(IV) as a plutonium reductant in Purex-process streams. In most cases the U(IV) used in these studies was prepared by reduction of uranyl nitrate solutions by aluminum-metal dust. The studies showed that U(IV) was sufficiently stable in Purex solvent to allow reasonable holdup time in process equipment. Since a small amount of nitrite is present in the organic feed stream, and nitrite oxidizes U(IV) rapidly, hydrazine must be introduced to the feed tank to destroy the nitrite. In process demonstration tests it was shown that plutonium reduction by U(IV) was sufficiently rapid and complete to assure adequate separation of plutonium from the product uranium stream. Reflux of plutonium by reoxidation and reextraction was no greater than in the ferrous sulfamate process.

Finlayson and Mowat[14] have described a method for the reduction of uranyl nitrate solutions to U(IV) by electrolytic techniques. Over 99.8% reduction to U(IV) was achieved in a continuous system by pumping uranyl nitrate solution through a series of seven electrolytic cells employing tantalum cathodes.

Precipitation of Plutonium Trifluoride

At the Savannah River Laboratory, plutonium is recovered from plutonium nitrate solutions by precipitation as the trifluoride.[15] A number of factors influence the physical properties and solubility of plutonium trifluoride: the plutonium valence, nitric acid and hydrofluoric acid concentrations in the precipitation media, the degree of agitation of the precipitate, and the manner in which the reactants are combined. Each of these factors was discussed in a previous issue of *Reactor Fuel Processing*.[16] The solubility product of PuF_3, calculated from several solubility measurements at appreciably different nitric and hydrofluoric acid concentrations, was $2.4 \pm 0.4 \times 10^{-16}$.

Conversion of Plutonium Dioxide to Plutonium Trichloride

A process for the preparation of metallic plutonium using a chloride intermediate is being developed at Hanford Atomic Products Operation.[17,18] The proposed process includes calcination of plutonium nitrate to PuO_2, chlorination of PuO_2 to $PuCl_3$, and electrolytic reduction of $PuCl_3$ to metallic plutonium. Development work[17] on this process has included the evaluation of a continuous fluidized-bed reactor for the conversion of PuO_2 to $PuCl_3$. The PuO_2 used in this study was produced by calcination of plutonium nitrate and contained 0.5 mole % sulfate. Chlorination was conducted at 450°C using undiluted phosgene as the chlorinating agent and fluidizing gas. Initial tests performed in a simple fluid-bed reactor were unsuccessful owing to extensive agglomeration of the fluid bed and channeling of the fluidizing gas. Successful operation was achieved in a fluid-bed reactor equipped with a mechanical stirrer. Conversion of

PuO_2 to $PuCl_3$ in a semicontinuous operation of the stirred-bed reactor was significantly greater when the oxide was introduced at the top of the reactor rather than at the bottom. Average conversion of PuO_2 to $PuCl_3$ was about 92%, which was considered satisfactory as a feed for electrolytic reduction to metal. For service in chlorinating environments at temperatures up to 500°C, Hastelloy C and glass appear most satisfactory, whereas preliminary evidence indicates that nickel is not suitable as a construction material.

Recent development on the chlorination of PuO_2 has been carried out in a stirred-bed reactor.[18] Tests were performed in a glass reactor capable of processing 500-g batches of PuO_2. A porous sintered-glass plate was used as the bed support and chlorinating-gas distributor. The stirrer was constructed of Hastelloy C and operated at 60 to 100 rpm. Both phosgene and carbon tetrachloride were used as chlorinating agents in these tests. Conversions of PuO_2 to $PuCl_3$ of greater than 90% were routinely achieved at 500°C using about 20% excess $COCl_2$ or 30% excess CCl_4. The $PuCl_3$ product was a finely divided free-flowing powder. The bulk density of the powder ranged from 2.3 to 2.9 g/cm^3. In all cases the $PuCl_3$ produced in these tests was suitable for feed to the electroreduction process.

Production and Properties of Uranium and Plutonium Carbides

Argonne National Laboratory (ANL) has carried on, for several years, a small effort on the synthesis of ceramic fuels, particularly carbides.[19–21] In the past few months, the program on the synthesis of carbide fuels has been expanded.[22] The technique[22–26] of synthesis which is now being studied is that of fluid-bed carburization of hydrided uranium–plutonium alloy with hydrocarbon–hydrogen gas mixtures to form (U,Pu)C. At the moderate operating temperatures of 700 to 900°C, volatilization of plutonium is not expected to be a problem.

Thermodynamics and reaction-rate evaluations have indicated the engineering feasibility of this process.[24–26] The minimum partial pressure of hydrocarbon gas for reaction of the gas with uranium metal is very low (~10^{-6} atm of methane at 1 atm of hydrogen pressure and 800°C), and no problems are imposed thereby. However, if the partial pressure of hydrocarbon gas is too high, $(U,Pu)_2C_3$ or carbon is formed under equilibrium conditions by the reactions:

$$CH_4 + 2(U,Pu)C \rightleftharpoons (U,Pu)_2C_3 + 2H_2$$

$$CH_4 \rightleftharpoons C + 2H_2$$

Because of inaccuracies in the data on free energy of formation of the carbides, the equilibrium methane-to-hydrogen ratio cannot be calculated with accuracy, especially for equilibrium with the mixed carbides. It is apparent from the chemical equations, however, that the use of high pressures would have a beneficial effect in allowing higher methane concentrations without resulting in deposition of free carbon or formation of higher carbides. At feasible operating temperatures and pressures, the allowable methane partial pressure is approximately proportional to the square of the total pressure.

At a given temperature and a given fluidizing velocity (conditions that cannot be widely varied), the methane throughput in a fluidized-bed reactor would be proportional to the partial pressure of methane. By operating at 800°C, 10 atm of total pressure, 0.4 atm of methane partial pressure, and 50% methane utilization efficiency (which has been attained in fluid-bed experiments), a carbide production rate of about 10 kg/hr could be attained in an 8-in.-diameter reactor. Under the above operating conditions, the product would be expected to be stoichiometric monocarbide.

Thermobalance experiments are being conducted to determine a more precise value of the equilibrium methane-to-hydrogen ratio for the reaction $2(U,Pu)C + CH_4 \rightleftharpoons (U,Pu)_2C_3 + 2H_2$ than can be calculated from the presently available free-energy data.[22–26] Runs were carried out in which uranium–20 wt.% plutonium alloy samples were reacted with propane–hydrogen or methane–hydrogen gas mixtures at 650 to 750°C. Most of the runs were conducted with a gas composition that would be expected to be in equilibrium with carbon or the sesquicarbide. However, only small amounts of sesquicarbide were formed in runs that were continued for several hours beyond the time (about 100 to 200 min) at which the formation of the monocarbide (as indicated by weight gain of the sample) had been completed. The low rate of formation of the sesquicarbide was attributed to a low rate of diffusion of carbon through the sesquicarbide reaction layer. In one experiment,[22] carried out at 770°C and atmospheric pressure, the equilibrium methane concentration in hydrogen for the reaction $2(U,Pu)C + CH_4 \rightleftharpoons (U,Pu)_2C_3 + 2H_2$ was demonstrated to be about 0.75 vol.%. Consequently the free-energy change for the reaction C + 2(U, 20 wt.% Pu)C ⇌ (U, 20 wt.% $Pu)_2C_3$ was calculated to be −4.4 kcal/mole of (U, 20 wt.% $Pu)_2C_3$.

Although preparations are now under way for fluid-bed synthesis of (U,Pu)C, the fluid-bed studies[22–26] up to now have been on synthesis of UC. Experiments have been conducted in a 1½-in.-diameter fluid-bed reactor at a pressure slightly above atmospheric pressure.[22–25] Results of some of the runs are shown in Table V-1. In these experiments 200 g of uranium rods was hydrided at 250°C to form finely powdered UH_3, suitable for fluidization. This powder was reacted with a propane–hydrogen gas mixture for 10 hr.

Table V-1 URANIUM MONOCARBIDE EXPERIMENTS IN A FLUIDIZED BED[22]

(200-g Scale; Run Duration, 10 hr)

Temp., °C	Propane in fluidizing gas,* vol.%	Product composition				
		Carbon		Oxygen		Uranium,† at.%
		At.%	Wt.%	At.%	Wt.%	
600	3	47.2	4.5	2.5	0.32	50.3
700	1.5	48.6	4.6	0.8	0.10	50.6
700	9	56.5‡	6.2‡	0.5	0.08	43.0

*The balance is hydrogen. The following C_3H_8 concentrations in hydrogen were calculated for C:H ratios equivalent to the equilibrium gas compositions in the systems $CH_4-H_2-UC-UC_2$ and $CH_4-H_2-UC_2-C$:

Temp., °C	C_3H_8 concentration, vol.%	
	$UC-UC_2$	UC_2-C
600	5.5	8.6
700	2.0	3.6

†Calculated by difference.

‡Carbon deposition on the reactor walls indicated that the product for this run probably had a high free-carbon content, as expected (see footnote * above).

A semiworks-scale reactor ($2\frac{1}{2}$ in. in diameter) has been installed for preparation of 2-kg batches of UC under the conditions: temperature, 700 to 900°C; pressure, 5 to 10 atm; and fluidizing gas, 2 to 10 vol.% methane in hydrogen. A reactor for preparation of (U,Pu)C is now undergoing shakedown runs, and a larger reactor for (U,Pu)C preparation is being designed.[22]

A fluid-bed process to convert $(U,Pu)O_2$ to (U,Pu)C is in the planning and design stage.[22]

A process has been developed at ANL for the production of PuC by direct reaction of the elements.[27] The process consists in charging plutonium into a graphite crucible liner, vacuum melting to cause reaction of the plutonium and graphite, and machining the remaining excess graphite from the button that is produced. The results of a series of reaction melts is given in Table V-2. In runs 5 through 8, it was shown that a 350-g batch of plutonium can be reacted to give a product with an average carbon analysis of 4.3 ± 0.2 wt.% by cycling between 1610 and 1660°C for 45 min. For the 1-kg batch size, the reaction time was increased and the product contained an average of about 4.6 wt.% carbon.

Typical product impurities are 225 ppm oxygen and 20 ppm nitrogen. The minor element impurities total about 1000 ppm and are essentially the same impurities that existed in the plutonium charged. About 95% of the plutonium in the original melt was converted to usable PuC. About 5% of the plutonium was in scrap material.

Plutonium carbide castings about 9 mm in diameter were produced by melting PuC in a bottom-pouring crucible-mold assembly provided with molds lined with vapor-deposited tantalum.

At Atomics International[28,29] single crystals of UC were grown in zone-refining experiments with an electron-beam melter in a vacuum ranging from 1 to 5×10^{-6} torr. Traverse rates were from 1 to 6 in./hr, and the chuck holding the specimen was rotated at rates of 0, 60, or 250 rpm. At 250 rpm the product was polycrystalline. With no rotation the product was a single crystal in which the subgrains showed less than a 2° mismatch; at 60-rpm rotation the product was also a single crystal, but the subgrains mismatched by 3 to 4°. As a result of uranium vaporization, the carbon concentration increased during zone refining by about 0.2 to 0.4 wt.% from the initial value of 4.7 to 4.8 wt.%. However, in one of the three runs at the highest traverse rate of 6 in./hr, no increase in carbon concentration was observed.

In zone-refining experiments[29] employing induction heating and an inert atmosphere (in which no uranium was lost by vaporization), approximate values were obtained on the distribution coefficients of carbon in solid liquid UC. The values obtained for the distribution coefficients were 0.2 for uranium-rich UC and 0.4 for carbon-rich UC. These values are in general agreement with published data on the U–C phase diagram but indicate better agreement with the higher UC–U solubility values obtained by Magnier and Accary.[30]

A paper by Leary et al.[31] summarizes work done at Los Alamos Scientific Laboratory in the past few years on refractory plutonium fuels. The equilibrium-phase relations between the four known carbides of plutonium, Pu_3C_2, PuC_{1-x}, Pu_2C_3, and PuC_2, and methods of preparing these compounds are discussed.

The vaporization behavior of UC in vacuum was studied at Pratt & Whitney Aircraft, CANEL, by the Langmuir evaporation technique.[32,33] Vaporization rates were measured in a vacuum thermobalance over the temperature range 2190 to 2525°K, and the partial pressures of the gaseous species were calculated. In this temperature range it was found that uranium monocarbide vaporizes congruently at a composition near $UC_{1.1}$ and that the vapor species are monatomic uranium, monatomic carbon, and C_2 and

Table V-2 PLUTONIUM REACTED IN GRAPHITE[27]

Run No.	Pu weight, g	Time at temp., min	Reaction temp., °C	Product, wt.% carbon				
				1	2	3	4	Average
1	190	8	1650–1975	9.12				9.12
2	330	45	1515	1.70	2.08			1.89
3	330	45	1560	3.13	3.11			3.12
4	330	45	1610	4.66	3.45			4.06
5	210	45	1520–1665	4.6	4.1			4.35
6	172	45	1610–1680	4.91	4.15	4.32		4.46
7	353	40	1610–1675	4.50	4.35			4.42
8	356	45	1610–1655	4.45	4.11			4.28
9	446	35	1745–1790	5.73	5.77			5.75
10*	976	90	1665	5.04	5.02	4.43	4.40	4.72
11*	1011	90	1640	4.83	4.87	4.76	4.77	4.81
12	1018	90	1610	4.59	4.28	4.71	4.66	4.56
13	1034	90	1655	5.11	4.44	4.92	5.17	4.91
14	990	90	1610	4.70	4.36	4.25	4.48	4.45
15	986	90	1610–1665	4.62	4.50	4.68	4.83	4.66
16	945	90	1610–1675	4.54	4.74	5.02	4.84	4.78
17	1018	75	1610–1675	4.59	4.71	4.58		4.63
18	1015	75	1610–1665	4.91	4.77	4.64	4.17	4.58
							4.43	
19*	1053	52	1610–1665	3.40	3.00	3.80		3.40

*Tall crucible.

C_3 molecules. With the assumption of a value of unity for the condensation coefficient in the Langmuir equation and with the data for the rate of vaporization, the partial pressure of uranium vapor, P_U, in equilibrium with $UC_{1.1}$ solid was calculated to be log P_U (atm) = $8.191 - 3.624 \times 10^4\ T^{-1}$ for temperature, T(°K), in the range 2190 to 2525°K. By the third-law technique, the heat of vaporization of $UC_{1.1}$ was calculated to be 235.1 ± 2.7 kcal/mole. The standard heat of formation of $UC_{1.1}$ at 298°K was calculated to be -21.2 ± 4.1 kcal/mole.

Production and Properties of Uranium and Plutonium Mixed-Anion Fuels

Work is being done by the United Nuclear Corporation and The Carborundum Company on preparation of uranium–plutonium monoxide type fuels containing carbon or nitrogen stabilizers.[34,35] The aim of this study is to develop for water-cooled thermal reactors a monoxide type fuel that has a higher thermal conductivity than $(U,Pu)O_2$ fuels and has corrosion resistance equivalent to $(U,Pu)O_2$ fuels. Attempts have been made to produce monophasic (U,Pu)(O,C), (U,Pu)(ON), and (U,Pu)(O,C,N), containing a high atom fraction of oxygen and a uranium-to-plutonium ratio of 9:1. Both carbon and uranium-metal reduction processes were employed in these studies. The reactions were carried out in a helium atmosphere or in vacuum.

To determine the maximum oxygen-atom fraction that could be obtained in (U,Pu)(O,C) type compounds, synthesis of such compounds was attempted with an intended oxygen-to-metal ratio of 1.0. The experimental procedure for the carbon reduction route consisted in ball-milling UO_2, PuO_2, and C for either 24 hr or 72 hr. Carbowax 6000 (0.4 wt.% of total solids) dissolved in benzene was added to the blends. When the resultant paste was stirred, 1/8-in.-diameter granules were formed. Ten grams of each batch of granules was heated in a tantalum-lined graphite crucible for 2 hr at 1750°C in flowing helium. The products[35] of four such runs contained 55 to 58 wt.% M(O,C) phase of the approximate composition $(U_{0.9}Pu_{0.1})(O_{0.58}C_{0.42})$. The effect of the additional grinding and the use of 0.5-μ UO_2 powder instead of the usual 3-μ UO_2 powder made no apparent difference in the product composition. Similar results[35] were obtained by forming pellets without a binder at 15,000 to 60,000 psi and heating the pellets under vacuum at 1650°C for 5 hr; the product contained 60 wt.% of an M(O,C) type phase containing an oxygen-to-metal ratio of approximately 0.6.

Since the maximum oxygen-to-metal ratio in (U,Pu)(O,C) type compounds was established at about 0.6 by the above experiments, other experiments were conducted that were aimed at obtaining the maximum amount of the (U,Pu)(O,C) phase, the intended product being $(U_{0.9}Pu_{0.1})(O_{0.6},C_{0.4})$. Thus far the best product obtained by carbon reduction in helium contained 86 wt.% of a (U,Pu)(O,C) phase with an oxygen-to-metal ratio in this phase of only 0.38. However, substitution of phenolformaldehyde resin for the usual carbon-powder reducing agent has produced a material[35] having 85 wt.% of a (U,Pu)(O,C) phase with an oxygen-to-metal ratio of 0.56.

Attempts to synthesize a high-oxygen material of the type (U,Pu)(O,N) were unsuccessful, apparently because of the low solubility of oxygen in the mononitride phase.[34]

The synthesis of (U,Pu)(O,C,N) compounds was undertaken utilizing the technique of uranium-metal reduction of $(U,Pu)O_2$. Some of the results are shown in Table V-3. Essentially single-phase material [>95% (U,Pu)(O,C,N)] was produced when the intended product was $M(O_{0.2}C_{0.2}N_{0.6})$. Products[35] containing greater than 90 wt.% of a (U,Pu)(O,C,N) phase were obtained by both metal and carbon reduction methods with

Table V-3 SYNTHESIS OF (U,Pu)(O,C,N) BY METAL-REDUCTION METHOD[35]

Reactants: UH_3, UO_2, UN, UC, PuO_2
Procedure: Blend 30 min in a 25-ml Spex Mixer, Press into 1/4-in.-diameter Pellets, Heat for 5 hr at 1650°C in Tantalum-Lined Graphite Crucible with a Helium Flow of 6 cu ft/hr

Intended composition*	Metallographic results, phases present, and amount, wt.%			Corrected M(OCN) composition†	M(OCN) lattice parameter, A
	M(OCN)	MO_{2-x}	Metal		
$M(O_{0.6}C_{0.2}N_{0.2})$	58	26	16	$M(O_{0.24}C_{0.42}N_{0.34})$	4.9270 ± 0.0006
$M(O_{0.5}C_{0.2}N_{0.3})$	73	16	11	$M(O_{0.26}C_{0.33}N_{0.41})$	4.9226 ± 0.0011
$M(O_{0.4}C_{0.2}N_{0.4})$	76	13	11	$M(O_{0.16}C_{0.31}N_{0.53})$	4.9173 ± 0.0003
$M(O_{0.3}C_{0.2}N_{0.5})$	88	9	3	$M(O_{0.15}C_{0.28}N_{0.57})$	4.9137 ± 0.0005
$M(O_{0.2}C_{0.2}N_{0.6})$	96	4		$M(O_{0.14}C_{0.24}N_{0.62})$	4.9126 ± 0.0007
$M(O_{0.2}C_{0.2}N_{0.6})$‡	96	4		$M(O_{0.16}C_{0.28}N_{0.62})$	

*M = $(U_{0.9}Pu_{0.1})$.
†Composition was calculated from point count, carbon content, and X-ray density. Nitrogen content assumed to be same as intended.
‡Pellets for water-corrosion tests.

product composition of approximately $M(O_{0.3}C_{0.3}N_{0.4})$ and $M(O_{0.3}C_{0.4}N_{0.3})$.

A product containing single-phase $(U_{0.9},Pu_{0.1})(O_{0.32}C_{0.68})$ disintegrated in a boiling-water corrosion test. A material containing 91 wt.% of $(U_{0.9}Pu_{0.1})(O_{0.21},C_{0.37},N_{0.42})$ did not change in weight or dimensions significantly after 137 hr in boiling water. However, on exposure[35] to 550°F water in an autoclave, this material disintegrated within 1 hr.

The synthesis of uranium nitride and uranium carbonitride in a fluidized bed at Harwell was discussed in a previous issue of *Reactor Fuel Processing*.[36] A more recent report of this work in an abridged form is now available.[37]

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